THE ANALYST

PROCEEDINGS OF THE SOCIETY FOR ANALYTICAL CHEMISTRY

SOCIETY SYMPOSIUM

AT the invitation of the Midlands Section the Society held a Symposium on "Food Analysis" at 2.30 p.m. on Thursday, February 18th, 1960, at the Council Chamber, Colmore Row, Birmingham. The Chair was taken by the President, Mr. R. C. Chirnside, F.R.I.C.

The following papers were presented and discussed: "Some Analytical Problems in the Dairy Industry," by K. A. Hyde, B.Sc., F.R.I.C.; "Routine Control in the Brewery," by W. A. Whitley, M.I.Biol.; "Control Tests in the Flour Milling Industry," by J. Williams, B.Sc., Ph.D., F.R.I.C.; "Quality Control Analysis of Pre-packed Foods," by G. Walley, B.Sc., F.R.I.C.

NEW MEMBERS

ORDINARY MEMBERS

Eric Addison, B.Sc. (Lond.); Herbert Antrobus; Cyril Coleman, A.R.I.C.; Michael Sidney Jeremy Dallas, B.A. (Oxon.); George Alfred Howard, M.Sc. (Manc.), Ph.D. (Cantab.); Vincent Husbands, A.R.I.C.; Morton H. Jacobs, B.A. (Penna.); Kenneth George Kimber, B.Sc. (Lond.), A.R.I.C.; William John Warren Lloyd, A.R.I.C.; Gordon Theo Matthews, B.Sc. (Lond.); John James McCafferty, B.Sc. (Lond.), A.R.I.C.; Allan Walter Chadaway Peacock, B.Pharm. (Lond.), F.P.S.; John Edward Pentelow, B.A. (Cantab.); Charles Edward Pietri, B.A. (N.Y.); Herbert Albert Schroeder, B.S. (Ohio).

JUNIOR MEMBER

John Graham Bennett, B.Sc. (Lond.).

DEATHS

WE record with regret the deaths of

Ernest Mostyn Hawkins
George Taylor
Reginald Frank Wright.

NORTH OF ENGLAND SECTION

THE thirty-fifth Annual General Meeting of the Section was held at 2.15 p.m. on Saturday, January 30th, 1960, at the "Nag's Head Hotel," Lloyd Street, Manchester. The Chairman of the Section, Dr. J. R. Edisbury, presided. The following appointments were made for the ensuing year:—*Chairman*—Dr. J. R. Edisbury. *Vice-Chairman*—Mr. J. Markland. *Hon. Secretary and Treasurer*—Mr. B. Hulme, Ch. Goldrei, Foucard & Son Ltd., Brookfield Drive, Liverpool, 9. *Members of Committee*—Messrs. R. Butler, J. F. Clark, W. Cule Davies, G. J. W. Ferrey, C. J. House and H. Pritchard. Messrs. F. Dixon and A. A. D. Comrie were appointed Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Section at which a paper entitled "Analytical Methods in Clinical Biochemistry" was given by H. Varley, M.Sc., F.R.I.C.

SCOTTISH SECTION

AN Ordinary Meeting of the Section was held at 7.15 p.m. on Friday, January 8th, 1960, at the Royal Society of Edinburgh, 22 George Street, Edinburgh, 2. The Chair was taken by the Chairman of the Section, Mr. A. N. Harrow, A.H.-W.C., F.R.I.C.

The subject of the meeting was "Infra-red Spectroscopy" and the following papers were presented and discussed: "Applications of Infra-red Spectroscopy," by L. J. Bellamy, B.Sc., Ph.D.; "An Application of G.L.C. - Infra-red Spectroscopy Technique," by D. M. W. Anderson, B.Sc., Ph.D., A.R.I.C. (see summaries below).

APPLICATIONS OF INFRA-RED SPECTROSCOPY

DR. L. J. BELLAMY said that the use of infra-red group frequencies for the identification of molecular structures was very well known and widely practised. Until recently this method had depended solely upon empirical data that had been slowly compiled by chemists and spectroscopists who had studied large numbers of related compounds. In recent years, however, several workers had attempted to rationalise these data and to interpret the frequency shifts that followed structural changes in terms of the alterations in bond polarity that would be expected from chemical considerations. As a result they now had a much better understanding of the nature of group frequencies and of the factors that controlled their positions. This had not only led to an improvement in the diagnostic powers of this method, but had also suggested new applications of infra-red spectroscopy in the determination of physical properties. For example, it was known that the changes in an X–HO monomeric stretching frequency with alterations in X depended directly upon the inductive properties of X. In consequence these frequencies in carboxylic acids could be related directly to their pK_a values. With multiple bonds such as the carbonyl group, other factors such as mesomerism and conjugation effects were also operative, and as these same factors in some cases controlled reaction rates, it was possible to use frequency shifts for the prediction of certain kinetic data.

The rationalisation of group-frequency data in this way had been extended beyond the basic interpretation of known data and had been used to devise compounds that could be expected to show anomalous or freak frequencies as a consequence of their local environment. The subsequent preparation and study of such materials had shown that the theory was well-founded. However, this approach was only applicable to those vibrations that were essentially mass insensitive. These comprised the higher-frequency bands and certain others involving the motion of hydrogen atoms. There remained large numbers of low-frequency bands in the "fingerprint" region that could not be treated in this way. However, this region was being developed in a new way by various specialists in specific classes of compounds. Vibrations, which in molecules of all types fell over a wide frequency range, often occurred in much narrower ranges within one class of compound. As a result, new correlations in this region were slowly being built up that were, for example, based only on sterols or carbohydrates and were applicable only within their limited context. Nevertheless such correlations were finding an increased use in organic chemistry.

Structural work on group frequencies had recently been reinforced by parallel studies on group intensities, and these promised to be very fruitful in the future as a further sensitive aid to diagnosis.

In the field of large molecules, infra-red spectroscopy was essentially a tool of the organic chemist. Advances therefore dealt either with the sharpening of the tool to make it more selective or more generally applicable or with those advances in chemistry itself that followed the direct application of the method. In this latter field a great deal of important work had been done, some facets of which could only be summarised in this lecture under headings such as orientation studies in polymers, crystallinity studies, the use of separation and infra-red methods in studying the chemistry of bacteria, hydrogen bonding, and so on. One field currently showing particular promise in this respect was that of stereochemistry, and some interesting results were available that allowed one, for example, to follow the various alterations in shape of large rings as the size was increased progressively.

An Application of G.L.C. - Infra-red Spectroscopy Technique

Dr. D. M. W. Anderson began his short paper by describing some of the advantages of obtaining, whenever possible, infra-red spectra in the vapour phase. Volatility considerations did impose limitations on the applicability of the technique, but its scope was nevertheless surprisingly wide. Complex mixtures could be quantitatively analysed once the components were known; the sensitivity and accuracy obtainable generally depended on the extent to which overlapping of the main absorption plates in the spectra of the components of the mixture did or did not occur.

The simple apparatus and technique used for examination of gas - liquid chromatography fractions (see *Analyst*, 1959, **84**, 50) were demonstrated, and results were presented to illustrate the sensitivity and scope of the technique. Possible applications to the investigation of sources of error in certain analytical procedures, to the simultaneous determination of mixed alkoxyl groups, to the analysis of *tert.*-butylated phenols and anisoles and to the analysis of other types of compound behaving anomalously in the Zeisel - Viebock reaction were discussed.

The twenty-fifth Annual General Meeting of the Section was held at 1.45 p.m. on Friday, January 29th, 1960, at the Grosvenor Restaurant, 72 Gordon Street, Glasgow, C.1. The Chair was taken by the Chairman of the Section, Mr. A. N. Harrow, A.H.-W.C., F.R.I.C. The following office bearers were elected for the forthcoming year:—*Chairman*—Mr. A. N. Harrow. *Vice-Chairman*—Mr. A. F. Williams. *Hon. Secretary and Treasurer*—Mr. J. Brooks, Analytical Research Section, Nobel Division, Imperial Chemical Industries Ltd., Stevenston, Ayrshire. *Members of Committee*—Messrs. R. A. Chalmers, A. L. Cochrane, F. J. Elliott, J. C. Jack, J. W. Murfin and A. O. Pearson. Messrs. C. B. Hackett and W. J. Murray were re-appointed Hon. Auditors.

The Annual General Meeting was followed by an Ordinary Meeting of the Section, at which a talk on "The Work of the Cereal Chemist: Some Aspects of New Techniques" was given by D. W. Kent-Jones, B.Sc., Ph.D., F.R.I.C.

WESTERN SECTION

The fifth Annual General Meeting of the Section was held at 5.45 p.m. on Friday, January 8th, 1960, in Cabot House, College of Technology, Ashley Down, Bristol. The Chair was taken by the Chairman of the Section, Mr. S. Dixon, M.Sc., F.R.I.C. The following appointments were made for the ensuing year:—*Chairman*—Dr. G. V. James. *Vice-Chairman*—Dr. F. H. Pollard. *Hon. Secretary and Treasurer*—Dr. T. G. Morris, Brockleigh, Clevedon Avenue, Sully, Glamorgan. *Members of Committee*—Messrs. R. E. Coulson, S. Dixon, B. W. Minifie, H. K. B. Rout and R. F. Stephens. Messrs. E. A. Hontoir and W. J. Williams were appointed Hon. Auditors.

The Annual General Meeting was followed by a Joint Meeting with the Bristol and District Section of the Royal Institute of Chemistry, at which a lecture on "Radiochemical Analysis" was given by J. H. Andrews, B.Sc., Ph.D., D.I.C., A.R.I.C. The Chair at this meeting was taken by the President of the Society, Mr. R. C. Chirnside, F.R.I.C.

THE ELWELL AWARD MEETING OF THE MIDLANDS SECTION

The Elwell Award Meeting of the Section was held at 6.30 p.m. on Thursday, January 7th, 1960, in the Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Chairman of the Section, Dr. S. H. Jenkins, F.R.I.C., F.Inst.S.P.

The following papers were presented and discussed: "The Polarographic Determination of Small Amounts of Tin and Lead in Zirconium and its Alloys," by R. T. Clark; "Neutron Activation Analysis of High-purity Aluminium," by D. Hazelby; "The Assay of Sodium Citrate and Sodium Potassium Tartrate by (*a*) Cation Exchange and (*b*) Non-aqueous Titrimetry," by M. L. Richardson.

At the beginning of the meeting it was announced that Mr. R. T. Clark was the winner of the Elwell Award for 1959. This Award consists of a silver cigarette box inside the lid of which is a plaque made of strips of titanium, zirconium, niobium and tantalum; it is to be held by the winner for one year. It will be awarded annually for the best paper on some aspect of analytical chemistry by a scientist under the age of 30 working or residing in the Section's area.

MIDLANDS SECTION AND MICROCHEMISTRY GROUP

A JOINT Meeting of the Midlands Section and the Microchemistry Group was held at 6.30 p.m. on Tuesday, January 12th, 1960, in The Mason Theatre, The University, Edmund Street, Birmingham, 3. The Chair was taken by the Vice-Chairman of the Microchemistry Group, Mr. C. Whalley, B.Sc., F.R.I.C.

The following paper was presented and discussed: "Micro Gas Analysis," by G. J. Minkoff, D.Sc., D.I.C. (see summary below).

MICRO GAS ANALYSIS

DR. G. J. MINKOFF said that, when considering the subject of gas analysis, say 10 years ago, it was possible to subdivide the activities involved into the categories of macro, semi-micro and micro, depending on whether the sample of gas was over 10 ml, between 0·5 and 3 ml or below 0·1 ml. The methods generally applied to the first group were mainly those of measuring the volume, or the pressure, of the sample after its treatment with certain reagents or absorbents. Errors due to preferential solubilities, and so on, were magnified when smaller volumes were being dealt with, so that methods with solid reagents only had been designed for smaller volumes of gas. For very small samples, special techniques, often involving use of microburettes, were required; more recently, the advantages of operating at very low pressures had been realised.

The subdivision was gradually becoming more difficult to maintain. For example, the detection of dangerous amounts of toxic substances, present in parts per million, might involve treating samples between 1 and 2 litres in volume by extremely sensitive methods. Again, the presence of 1 to 2 per cent. of inflammable material might well lead to the possibility of an atmosphere becoming explosive; the sample was still large, but the sensitivity might be less. These two fields differed in that the former usually called for tests specific to individuals, whereas the latter could rely merely on properties associated with the available heat of combustion.

During the last 10 years, the discovery and improvements of gas chromatography and infra-red and mass spectrometry, and the refinements of numerous physical methods for analysing gaseous mixtures had affected both the selectivity and the sensitivity. For example, what might once have been reported as "30 per cent. paraffins," might now be resolved into, say, 30 components, each present in 1 per cent. concentration. Hence the detecting system needed to be 30 times more sensitive in order to make full use of the information available. Fortunately, the two aspects had gone hand in hand, particularly in the field of gas chromatography. There, the increasing fractionation efficiency had been paralleled by the development of detectors such as the katharometer, the Scott flame, flame ionisation and β-ray ionisation detectors (the last-named being less sensitive to small molecules).

The lecturer reviewed the main features of the chemical methods as well as those of the physical ones, the topics covered including low-pressure gas-analysis systems, toxic and hazard detection and suitable physical properties permitting, for example, the magnetic estimation of oxygen. More detailed discussion of gas chromatography, mass spectrometry and infra-red spectrometry (both dispersive and non-dispersive) showed that these methods often had sensitivities comparable to (and often better than) those of conventional micro methods. The inherent limitations were also described.

MICROCHEMISTRY GROUP

THE twenty-third London Discussion Meeting of the Group was held at 6.30 p.m. on Wednesday, January 27th, 1960, in the restaurant room of "The Feathers," Tudor Street, London, E.C.4. The Chair was taken by the Vice-Chairman of the Group, Mr. C. Whalley, B.Sc., F.R.I.C.

A discussion on "Treatment of Inorganic and Organic Materials for the Determination of Metals" was opened by C. Whalley, B.Sc., F.R.I.C.

BIOLOGICAL METHODS GROUP

An Ordinary Meeting of the Group was held at 7 p.m. on Wednesday, January 20th, 1960, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chair was taken by the Chairman of the Group, Dr. J. I. M. Jones, F.R.I.C.

The following paper was presented and discussed: "Antibiotic Assays in Body Fluids," by Professor L. Garrod, M.A., M.D., F.R.C.P.

Analytical Methods Committee

ESSENTIAL OILS SUB-COMMITTEE

Fiore Method for Determining Linalol: Amendment

In 1957, the Analytical Methods Committee published a Report by its Essential Oils Sub-Committee on The Determination of Linalol in Essential Oils.[1] The respective merits of the Fiore and Glichitch methods were discussed, and, because the evidence then available indicated that the latter method was the more reliable, it was recommended as the method of choice.

With the development in recent years of gas - liquid chromatography, a useful technique has been provided for investigating the course of certain chemical reactions. This technique was applied by Holness[2] to studying the reactions of both the Glichitch and Fiore methods for determining linalol (both natural and synthetic), and it was shown that, of the two methods, the products of the Fiore reaction were much the simpler, although both methods gave repeatable results. However, it was concluded that potential sources of error are greater in the more complex Glichitch reaction; further, Holness[2] has shown that results for linalol by the Glichitch method are consistently incorrect, being about 4 per cent. lower than the true value, whereas results by the Fiore method are only about 1 per cent. lower than the true value. In linalol-containing oils, compensating errors tend to narrow the differences in apparent linalol content as determined by the two methods.

The Essential Oils Sub-Committee, on whose behalf these experiments were performed, has given careful consideration to these findings and it has been unanimously agreed that the conclusions reached in the 1957 Report should be reversed, *i.e.*, that the Fiore method should now be recommended as the method of choice.

References

1. Analytical Methods Committee, "The Determination of Linalol in Essential Oils," *Analyst*, 1957, **82**, 325.
2. Holness, D., *Ibid.*, 1959, **84**, 3.

The Determination of Trace Quantities of Silver in Trade Effluents

Report to the Analytical Methods Committee of work carried out at Oxford by

T. B. PIERCE

under the supervision of Dr. H. Irving

Introduction

Silver adversely affects the anaerobic bacterial processes in sewage treatment, and it is toxic to fish and other aquatic life. A need has therefore arisen for the determination of small amounts of silver in water that may have become contaminated with trade effluent, since local authorities may require a limit on the amount discharged. Any proposed method must be capable of determining amounts of silver down to 0·01 p.p.m.

Many methods have been proposed for determining small amounts of silver, but few of these are reliable in the presence of organic material or at the concentration levels now imposed. Interference from common metals, such as copper, lead and iron, has not always been overcome. For example, in Jelley's method,[1] said to be sensitive to 50 μg in a 50-ml sample, silver is reduced in ammoniacal solution in the presence of gelatin and the colloidal metal is determined colorimetrically; copper, cobalt, nickel, cadmium and iron interfere. Members of the Joint Committee of the Association of British Chemical Manufacturers and the Society for Analytical Chemistry on Methods for the Analysis of Trade Effluents who have investigated this method found it insufficiently sensitive and adversely affected by organic matter and foreign metals.[2]

Procedures involving absorptiometry of its complexes with dithizone or *p*-dimethylaminobenzylidine rhodanine[3] have been claimed for determining silver down to 0·5 and even 0·1 p.p.m. As will be shown later, these procedures fail when organic material and substantial amounts of other metals are present. In any event some measure of concentration by a factor of 10- to 100-fold would be required before the methods could be applied to samples of water containing only 10 μg of silver per litre.

Heller, Kuhla and Machek[4] have described the construction and operation of a still designed to concentrate trace metals from several litres of natural waters before their determination polarographically or otherwise. Caldwell and McLeod[5] recovered 3·06 mg from a total of 3·29 mg of silver in a 40-litre sample (concentration about 0·1 p.p.m.) by "occlusion" on the gelatinous precipitate obtained by adding ammonia, mercuric chloride, hydrochloric acid and magnesium metal; the element was determined gravimetrically in the form of metal after cupellation. There are obvious reasons for avoiding methods of this kind, which demand, *inter alia*, large volumes of sample. In the absence of special apparatus and dust-free rooms, sample volumes greater than 1 litre would appear to be excessive.

Preliminary investigations

In preliminary work[2] the separation of silver with or without previous destruction of organic matter was attempted by chromatography on Zeo-Karb resin, silica gel, aluminium oxide and paper and then elution with various combinations of organic solvent and aqueous acids (or ammonia). Other procedures examined were (*a*) Aldridge's method for the separation of silver as the cyanide and then indirect determination of silver by measuring the amount of cyanide obtained on distillation,[6] (*b*) colorimetric determination of silver after reduction with aldehyde or sucrose,[7] (*c*) separation as silver iodide and then liberation of iodine and its determination absorptiometrically in solution in carbon tetrachloride, (*d*) reduction to metallic silver on paper fibre[8] and (*e*) coagulation and separation of the silver - rhodanine lake at the interface of an immiscible solvent.

Some of these methods had a limited success, but an extremely serious difficulty was encountered in the readiness with which silver is adsorbed on and not subsequently removed from glass (both soft and Pyrex), porcelain, silica and possibly calcium sulphate.[2] Hamence[2]

has confirmed the adsorption of silver on calcium sulphate and has emphasised the need for solubilising any such solid residue from wet oxidation before proceeding with the final determination. Gorsuch[9] has recently shown that up to 47 per cent. of silver can be retained on ignition of its nitrate at 500° C for 16 hours in a silica crucible, but his data (*loc. cit.*, Table XX) point to a maximum loss of 5 per cent. in wet oxidations involving a total weight of 10 μg of the element. However, it is important to realise that if such a loss were due simply to adsorption on the reaction vessels, the weight of silver adsorbed might be of the same order when only a total of 1 μg of metal is involved, in which event the loss could amount to as much as 50 per cent. We have confirmed the reality of such losses when 1 μg or less of silver is manipulated in ordinary laboratory glassware and have shown that they are significantly reduced on giving all such glassware a water-repellent coating of silica by treatment with a suitable reagent (see p. 174).

Sherratt[2] has examined Sandell and Neumayer's method[10] for determining silver after wet oxidation of organic matter with a mixture of sulphuric and nitric acids. He established the conditions for preparing reproducible standard curves for minute amounts of silver in distilled water, a solution of rhodanine in acetone and alcohol being used as colour-forming reagent. Interference by common metals and especially by excess of reagent could be suppressed by controlling the acidity. Nitric acid was found to be preferable to sulphuric acid for this purpose, but it must be freshly prepared by distillation from urea to remove all traces of nitrous acid. The extraneous colour from 1 ml of 0·1 per cent. rhodanine solution could be suppressed by using 4 ml of freshly prepared *N* nitric acid diluted to 50 ml with distilled water. The limitations of the method for our purposes are clearly shown by the results in Table I.[2]

TABLE I

RECOVERY OF SILVER FROM 100 ml OF DRINKING WATER* TO WHICH 0·05 g OF QUEBRACHO TANNIN HAD BEEN ADDED

Metal added, μg							
Silver	0	5	20	0	5	10	20
Lead	0	0	0	100	100	100	100
Mercury	0	0	0	100	100	100	100
Iron	0	0	0	100	100	100	100
Optical density†	0·015	0·032	0·087	0·030	0·032	0·048	0·102
Optical density corrected for blank	—	0·017	0·072	—	0·002	0·018	0·072
Silver found, μg	—	2·5	11·2	—	0·2	2·7	11·2

* Hardness of the drinking water was 120 p.p.m. of calcium, as $CaCO_3$, and 44 p.p.m. of magnesium, as $MgCO_3$.

† The calibration curve (1-cm cell, Ilford No. 604 filter) was prepared for 0 to 25 μg of silver in a final volume of 25 ml.

We have also carried out some work on the determination of silver by the rhodanine method and do not find it sufficiently reliable at the concentration levels required. The results appear to be extremely sensitive to changes in the acidity of the final solution.

SCOPE OF THE WORK REPORTED

In view of the proved inadequacy of existing procedures a new approach was called for. The alternatives would appear to be a search for a new procedure of adequate sensitivity or a study of concentration techniques that would allow some well tried analytical procedure to be used as a finish.

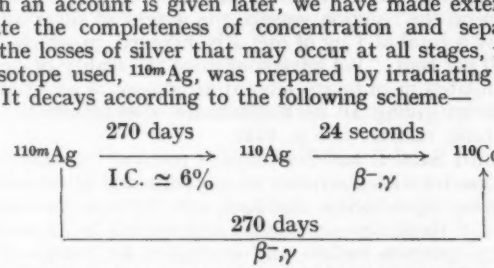
It would be unjustifiably optimistic to hope to improve the sensitivity of existing absorptiometric procedures by the necessary factor of between 10 and 100 times, except by fortuitous discovery of an entirely new type of reagent. On the other hand neutron-activation analysis would appear to provide the required sensitivity in that a sample of only 1 ml should suffice if the estimated ultimate sensitivity of 5×10^{-9} g could be realised.[11] This would, however, involve irradiation in a nuclear reactor for a period of 1 month, but, although the subsequent chemistry could be greatly simplified or indeed replaced by γ-ray spectrometry, it was thought that a speedier and less specialised technique would be more generally acceptable.

The problem thus resolves itself into an examination of three separate stages, *viz.*, (*i*) concentration, (*ii*) separation from interfering elements and (*iii*) final determination.

Several possibilities were examined for each stage and the final procedure, which is given in full in the Appendix, p. 174, represents a compromise between acceptable accuracy and general convenience.

USE OF RADIOACTIVE SILVER—

As well as the preliminary trials of a new method for determining traces of silver radiometrically, of which an account is given later, we have made extensive use of radioactive silver to investigate the completeness of concentration and separation procedures and especially to trace the losses of silver that may occur at all stages, more especially through adsorption. The isotope used, ^{110m}Ag, was prepared by irradiating Specpure silver wire in the Harwell pile. It decays according to the following scheme—



It is convenient to use both on account of its long half-life and because end-window counting for β-rays and scintillation counting for γ-rays could be used as appropriate. Counting rates up to 6000 disintegrations per minute per μg of silver were easily obtainable.

CONCENTRATION PROCEDURES—

If physical concentration by distillation[4] is to be rejected, the possibilities presented by co-precipitation, the use of ion-exchange resins and the technique of solvent extraction must be explored. We have made studies in each of these fields with "labelled" silver throughout. It will be obvious that if the concentration stage can also be made selective or, ideally, specific for silver, the second stage, that of removing elements likely to interfere in the final determination, will be greatly simplified and over-all losses may be greatly reduced.

(*a*) *Co-precipitation techniques*—The adsorption of silver on amino-mercuric chloride[5] has already been mentioned. Sandell and Neumayer recommend the collection of silver on tellurium,[10] and the same procedure has been used recently by Hamagudi and Kuroda.[12]

The low solubility of silver sulphide suggests its possible collection on a suitable carrier sulphide. If this were a sulphide of group 2, the precipitation in acid solution would have the additional advantage of breaking down most soluble complexes of silver with proteins and their degradation product and also of minimising surface adsorption on glassware. Both thioacetamide and washed hydrogen sulphide gas were used as precipitants. Some typical results are shown in Table II; they indicate that recoveries of 99 per cent. or better are easily attainable. Co-precipitation on tellurium, produced by adding first sodium tellurite and then stannous chloride to a sample of water containing traces of silver, was found to be extremely effective even in the presence of tannin (to simulate organic matter) up to a concentration of 5 g per litre.

TABLE II

EFFICIENCY OF VARIOUS MATERIALS FOR COLLECTING SILVER BY CO-PRECIPITATION

Carrier	Concentration of hydrochloric acid, *N*	Silver precipitated, %
HgS	≤4	98·5
CuS	≤4	99
PbS	0·1	95
Te	≤4	99
Te	≤4*	99

* Containing up to 5 g of tannin per litre.

The main disadvantage of scavenging with a sulphide of copper or mercury is that it will also collect all group-2 metals. The tellurium precipitate was found to carry down both mercury and copper. Both these metals interfere strongly in the absorptiometric determination of silver with dithizone,[3] and it has been stated that tellurium itself will give a dithizone complex in acid solution,[13] although we were unable to confirm this unequivocally.

(*b*) *The use of ion-exchange resins*—There would appear to be nothing to be gained in selectivity by attempting to concentrate the metals present in polluted water with a cation-

exchange resin. On the other hand, the use of anion-exchange resins presents some interesting possibilities. Thus silver is known to be adsorbed by such resins in the chloride-ion form with values of the distribution coefficient, K_D, ranging from about 1000 in neutral solution to zero in 10 *M* hydrochloric acid.[14] These differences are sufficient to permit its separation from palladium, which is retained firmly even in 10 *M* acid.[15] Marcus[16] reports values of log K_D ranging from 5·15 to 0·95 for the adsorption of silver on Amberlite IRA-400 from 0·004 to 5·50 *M* solutions, respectively, of sodium thiosulphate. The adsorption of silver from cyanide solutions has also been reported.[17]

Extraction from a cyanide medium should have many advantages, since the high stability of this ion would ensure that silver would be adsorbed irrespective of the form in which it might originally be held as a complex in aqueous solution. The danger of losses by adsorption on containers would also be reduced. Further, since comparatively few metals form stable complex cyanides the process of concentration would also achieve a useful separation.

With radioactive silver and Amberlite IRA-400 in its cyanide form we found the values shown below for the distribution coefficient at various concentrations of cyanide in the aqueous phase—

Concentration of cyanide in aqueous phase, *M*	0·25	0·50	1·00	1·50	2·00	3·00	4·00	5·00
Log K_D	4·04	3·53	3·03	2·70	2·42	1·87	1·44	0·95

These figures imply that, if 100 ml of water containing 1 μg of silver were to be equilibrated with 10 g of resin in the cyanide form, such that the concentration of cyanide ion in the aqueous phase was 0·25 *M* or less, 99 per cent. or more of the silver would be adsorbed. This was confirmed by experiment with radioactive silver, and excellent decontamination from a number of other elements was shown to be possible. For example, it was found that copper, lead and mercury could be completely eluted in about twenty column-volumes of 2 *M* potassium cyanide without appreciable loss of silver.

The subsequent quantitative removal of silver from a cyanide resin was found to present unexpected difficulties. Elution with 6 *M* potassium cyanide was certainly effective, but the resulting solution was unpleasant to handle and contained large amounts of ions that would seriously interfere with the subsequent determination of silver. Strong ammonia or 5 per cent. hydrochloric acid was ineffective as eluting agent, and large volumes of acetone - hydrochloric acid mixtures were needed to achieve quantitative elution of silver. Dry ashing of the resin was found to lead to the loss of up to 50 per cent. of the silver. Wet ashing with concentrated sulphuric acid alone induced partial carbonisation, and, although the use of a mixture of concentrated nitric and perchloric acids was completely effective, the operation was time-consuming. The most convenient way of removing silver quantitatively from a cyanide resin was to warm it with concentrated nitric acid in an evaporating basin. The contents of the basin were then evaporated to dryness under an infra-red lamp, and the residue was treated with *N* sulphuric acid, any resin remaining unattacked being removed by centrifugation.

Silver was found to be quantitatively adsorbed on an anion-exchange resin in the chloride form from a solution containing a large excess of lead, copper, iron, mercury and tannin. Elution was readily carried out with ammonium hydroxide. This procedure appears to have some advantages over the cyanide method, for it produced the desired concentration of silver in a solution containing no large concentration of salts or interfering ions. However, the value of K_D is rather critically dependent upon the concentration of chloride ion in the aqueous phase, which reduces the percentage of silver adsorbed by the resin when present at even quite low concentration. The procedure therefore cannot be recommended for use with effluents of variable or unknown chloride ion content.

(*c*) *Solvent extraction*—The immense advantages of this technique for purposes of concentration and separation hardly need emphasising. In order to extract ionic silver it is first necessary to convert it to an uncharged complex by co-ordination with a suitably charged ligand. The chemistry of silver suggests that co-ordination through sulphur would be preferable to co-ordination through nitrogen and that phosphorus or arsenic would be even better as donor atoms.[18] Few suitable complexing agents based on phosphorus or arsenic have been examined, and the choice between the sulphur compounds BAL (2:3-dimercaptopropanol) and dithizone (1:5-diphenyl-3-mercaptoformazan) was made on the basis of the difficulty of removing silver from its complex with the former and the greater selectivity

of the latter. Since the distribution of metal between organic and aqueous phases is determined for the weakly acidic reagent dithizone (HDz) by the equilibrium—

$$\frac{[M^{n+}]_{aq.}}{[MDz_n]_{org.}} = \frac{K[H^+]^n_{aq.}}{[HDz]^n_{org.}}$$

considerable selectivity may be superimposed upon the concentration stage by an appropriate choice of pH and by the addition of masking agents to the aqueous phase.[19] The same favourable factors are operative in reverting ionic silver from its dithizone complex.

The solvent extraction of dilute solutions of silver in sulphuric acid (down to 0·01 p.p.m.) was studied with the aid of "labelled" silver. When a strong solution of dithizone in carbon tetrachloride was used (100 mg per litre), it was found that the proportion extracted did not fall below 98 per cent. until the acidity of the aqueous phase was as high as 12 *N* and that for lower acidities the extraction of silver was effectively quantitative in a single equilibration. Tannic acid, which was used to simulate organic matter present in a trade effluent, was found to have no adverse effect at concentrations up to 5 g per litre, and over 95 per cent. of silver was removed in one pass from such a solution containing 20 μg of silver per litre. At any given pH the extraction of silver takes place in preference to that of mercury, copper, zinc, lead, etc.; if the extraction is continued until a further portion of (diluted) dithizone remains green, the removal of silver will certainly have been complete. The high stability of the silver - dithizone complex and the favourably high distribution coefficient from strongly acidic media have the further important advantage that the metal can be extracted from aqueous solutions in which it may be present as complexes with amino acids or other breakdown products of proteins. Considerable concentrations of chloride ion were found not to inhibit the extraction.

By using a synthetic effluent containing, besides silver, tannin, mercury, lead, copper and iron dissolved in ordinary tap-water (see p. 167) it was shown that after acidification with sulphuric acid to approximately 0·5 *N*, three extractions with 5-ml portions of dithizone solution (100 mg per litre) were sufficient for the quantitative removal of silver from up to 500 ml of sample. The procedure is therefore admirably suited for the primary concentration of silver by a factor of 10 or better; it has the added advantages of speed, the use of readily accessible apparatus and reagents and the immediate separation of silver from much organic matter and from the alkaline-earth metals, which, in any wet-ashing procedure, provide a bulky residue of solids on which the silver is readily and strongly adsorbed.

In a few experiments with various synthetic effluents a solid sometimes separated at the water - carbon tetrachloride interface. Measurements of its activity showed it to contain appreciable quantities of silver. Whenever such a scum appears it should be transferred with the organic phase for further treatment.

THE SEPARATION STAGE—

The choice of method to be used in the final determination of separated silver must influence the extent to which a preliminary separation of interfering elements will be required, and it will also influence the choice of the primary method of concentration. After some experience of the rhodanine method for silver we decided on an absorptiometric finish for silver, with dithizone as the colour-developing reagent. Merkupral (tetramethylthiouram disulphide) has recently been recommended[20] for the determination of silver in ores and is said to be specific for this element. The procedure depends upon the bleaching by silver ions of the colour of the Merkupral - copper complex, and the sensitivity does not appear to be so great as that of the dithizone method, which can be made as specific by a suitable choice of reaction conditions.

Exhaustive extraction by dithizone of an aqueous phase 0·5 *N* with respect to sulphuric acid will remove varying amounts of mercury, copper and palladium in addition to the whole of the silver. The presence of large amounts of palladium is not expected in trade effluents, and up to a 10-fold excess will not invalidate the final determination of silver.

With radioactive silver we confirmed that, when an organic solution containing the dithizonates of silver, mercury and copper was shaken with an acidified solution of ammonium thiocyanate, the silver was reverted into the aqueous phase and that the process was quantitative for 2 per cent. ammonium thiocyanate solution provided the concentration of the (sulphuric) acid was below 2 *N*. Other experiments showed that copper and mercury

remained in the organic phase. The acidified ammonium thiocyanate was also found to dissolve any interfacial scum containing silver, presumably as an anionic complex.

Before the final absorptiometric determination of silver it is necessary to remove all thiocyanate ions. This was most conveniently done by adding sulphuric acid and evaporating to fumes under an infra-red lamp. The residue could then be dissolved quantitatively in a little nitric acid to which urea and hydroxylamine were then added to prevent any oxidation of dithizone by nitrous fumes in the final stage.

As previously stated, radioactive silver was used to study the completeness of every stage and combination of stages in the proposed procedure. It was soon discovered that losses of silver by adsorption on the walls of the vessel could be extremely serious. For example, losses up to 50 per cent. occurred by simply shaking a solution of silver nitrate (1 p.p.m.) in a clean stoppered Pyrex-glass tube. Removal of this adsorbed silver was difficult, even with boiling nitric acid. Adsorption on polythene and porcelain was equally serious. Adsorption on a fused-silica surface was, however, small, and it was established that the losses due to adsorption on glass could be materially reduced by coating all the surfaces likely to come into contact with silver with a layer of silica applied by means of a commercial "silicone" preparation (see p. 174). This is regarded as an essential part of the recommended procedure.

FINAL DETERMINATION OF SILVER—

(*a*) *Absorptiometric determination*—This final stage can be carried out (*i*) by measuring the absorption due to the yellow silver dithizonate complex at 462 mμ, (*ii*) by measuring the decrease in the absorption of a standard solution of dithizone at its maximum of 620 or 450 mμ and (*iii*) by a reversion procedure.[21] Determinations of silver in the range 0 to 1 μg were studied with use of a dilute solution of dithizone in carbon tetrachloride (5 mg per litre). In view of the limited volume of extract available it was necessary to use micro-cells with a light path of 10 mm and holding about 0·5 ml. When a Spekker absorptiometer was used, the Ilford spectrum orange No. 607 filters (with maximum transmission near 600 mμ) were found to be the most suitable for measuring the concentration of residual dithizone (method (*ii*)), but the mixed-colour determination of silver dithizonate (wavelength (max.) at 462 mμ) in the presence of excess of dithizone (method (*i*)) was found to be unreliable owing to the closeness of this maximum absorption to the secondary absorption peak (450 mμ) of dithizone. Moreover, the best Ilford filter available for this has a comparatively low transmission, and over-all sensitivity is poor. We were reluctant to rely on a "mono-colour" method, which would entail stripping excess of dithizone from the mixture with silver dithizonate.

If the final solution to be determined still contained similar amounts of copper or mercury the reversion method could be used to advantage. For if C_s, C_c, C_m and C_d are the concentrations and e_s, e_c, e_m and e_d are the molecular extinction coefficients of silver dithizonate, copper dithizonate, mercury dithizonate and dithizone excess, respectively, the total absorbancies A_M and A_R before and after shaking with acidified ammonium thiocyanate (which will revert only silver dithizonate to an equivalent amount of dithizone) will be given by—

$$A_M = e_sC_s + e_cC_c + e_mC_m + e_dC_d$$

and—

$$A_R = e_dC_s + e_cC_c + e_mC_m + e_dC_d$$

whence the reversion value

$$\Delta A = (A_R - A_M) = C_s(e_d - e_s)$$

As predicted, the reversion curve (the plot of ΔA against the concentration of silver taken) was linear over the range 0 to 2 μg. The reversion method has the advantage that the slope of the calibration curve can readily be checked by carrying out the reversion procedure with a single known concentration of silver—since the calibration curve passes through the origin. A greater advantage in practice is the circumstance that the position of the calibration curve does not depend upon the concentration of dithizone used, so that the problems involved in preparing or maintaining solutions of this notoriously unstable reagent are largely circumvented.

In preliminary work, during which anion-exchange resins (see p. 168) were considered as a means of concentrating silver, it was foreseen that the final determination of silver might have to be made in the presence of small amounts of copper. We therefore re-examined

the method recommended by Leopoldi,[22] in which use is made of the fact that silver will displace copper from the violet cupric keto-dithizonate to give a series of mixed colours ranging from violet to yellow. We confirmed that the method was excellent for the determination of silver in the presence of copper, but we preferred the simple method (*ii*) or the reversion procedure (*iii*), because (*a*) the colour changes are clearer if visual matching of samples is used (*q.v.*), (*b*) the standard solution of copper dithizonate appeared to be photosensitive and needed frequent re-standardisation and (*c*) absorptiometric determination of the optical density of mixed-colour solutions involved the use of the Ilford spectrum blue filter and the sensitivity and reproducibility were less satisfactory than in the other methods examined.

The final procedure for the determination of silver, *viz.*, solvent extraction to concentrate the element, selective reversion to separate it from interfering elements and an absorptiometric determination with dithizone, is fully described in the Appendix. Over the range 0 to 1 μg in the final solution an accuracy to within ± 10 per cent. was achieved under optimum conditions; this would appear to be adequate for the proposed lower limit of 1 p.p.m. when a 100-ml sample is used. With higher concentrations of silver there is an appreciable increase in accuracy.

(*b*) *Flame photometry*—Through the courtesy of Messrs. Unicam Instruments Limited we were able to study the determination of silver in aqueous solution on the SP900 flame spectrophotometer. At the appropriate wavelengths of 328 and 338 mμ it was found that this method of analysis was inferior to absorptiometric procedures in the microgram range owing to the high water background at these wavelengths. We have not examined the possibilities of atomic-absorption spectroscopy.

(*c*) *Radiometric methods*—Although it was considered preferable to develop a method that did not involve the use of radiometric measurements in its final form, some preliminary experiments have suggested that a new method for the determination of silver could be developed from the following considerations.

Let us suppose that a solution of silver keto-dithizonate in an organic solvent is prepared from radioactive silver and completely freed from excess of unreacted silver or dithizone. If this solution is equilibrated with an aqueous solution containing a much smaller amount of inactive silver, the isotopes will exchange and the amount of radioactivity in the aqueous phase will be a measure of the amount of silver originally present there. If the specific activity of the silver available is sufficiently high, an extremely sensitive method becomes available for the determination of traces of silver.

Specifically, let—

S_a = number of moles of radioactive silver originally in the organic phase,
S_i = number of moles of inactive silver originally present in the aqueous phase,
X_i = the number of moles of silver that, at equilibrium, have gone from the organic to the aqueous phase,
$[H^+]$ = concentration of acid in the aqueous phase and
V_o and V = the volumes of the organic and aqueous phases.

The partition equilibrium of silver dithizonate may be represented by the equation—

$$AgDz_{org.} + H^+_{aq.} \rightleftharpoons Ag^+_{aq.} + HDz_{org.}$$

whence—
$$\frac{[AgDz]_{org.}}{[Ag^+]_{aq.}} = K\frac{[HDz]_{org.}}{[H^+]_{aq.}}$$

From the above—
$$[AgDz]_{org.} = (S_a - X_i)/V_o$$
$$[Ag^+]_{aq.} = (S_i + X_i)/V$$
$$[HDz]_{org.} = X_i/V_o$$

whence—
$$(S_a - X_i)/(S_i + X_i)X_i = K/[H^+]V = K' \text{ (constant).}$$

The total activity in the system is proportional to S_a. The total amount of silver in all forms is $(S_a + S_i)$ and the amount present in the aqueous phase at equilibrium will be $(S_i + X_i)$. The activity of the aqueous phase will thus be proportional to the quotient $(S_i + X_i)/(S_a + S_i)$. It is not difficult to show that, when conditions are properly chosen

and S_i is much smaller than S_a, it follows that the counting rate of the aqueous phase will be proportional to S_i and to the specific activity of the radionuclide taken. Fig. 1 shows the results of equilibrating active silver dithizonate (counting rate about 1000 disintegrations per minute per ml in a liquid counter) with 12 times its volume of an aqueous phase 0·5 *M* with respect to sulphuric acid and containing varying small amounts of inactive silver. It is clear that the experimental results conform to those predicted theoretically. The calibration graph is linear over the range 0 to 1 μg of silver, and it should be quite feasible to determine amounts as low as 0·01 μg, provided the equilibrations can be carried out reproducibly. Certain experimental difficulties remain to be overcome before this method can be confidently recommended, but its potentialities are considerable.

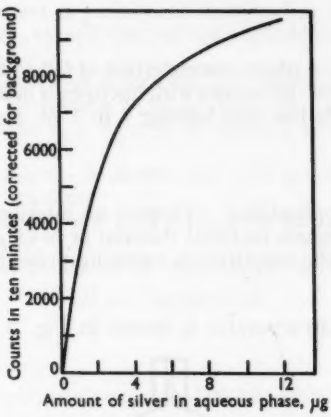


Fig. 1. Curve for the equilibration of radioactive silver dithizonate with 12 times its volume of an aqueous phase 0·5 *M* with respect to sulphuric acid and containing different small amounts of inactive silver

RADIOCHEMICAL CHECK ON THE OVER-ALL EFFICIENCY OF THE RECOMMENDED PROCEDURE—

We have stated that radioactive silver has been used to establish the completeness of individual stages in the procedure finally recommended. Although we have established by the use of ^{110m}Ag that the whole process of isolating and separating silver can be carried out without loss, so that the recommended procedure does not require the use of radioactive isotopes, when counting equipment and a supply of the long-lived silver isotope are available the reliability of the entire process can be enormously enhanced for the occasional or less experienced operator by application of the principle of isotopic dilution.

Let us suppose that a known amount of silver, X μg, of specific activity, f, is added to the sample containing an unknown amount of silver, x μg. The entire analytical procedure is carried out up to the point when the total amount of silver present is calculated from the absorbancy of the sample of silver dithizonate. The activity of the silver present in this sample is then measured radiometrically (after reversion to an aqueous phase of the appropriate composition to avoid errors due to energy absorption). Had there been no losses at any stage the activity would clearly be fX. From the measured activity the over-all chemical yield is calculated, and the measured value of the sum (X + x) corrected if necessary. With obvious modifications this procedure can be of great value in detecting and correcting for adventitious losses in what must inevitably be a rather elaborate series of operations. Since it is possible to obtain silver of high specific activity, it is feasible to make the quantity X similar to or smaller than the weight, x, of silver in the unknown. We have not thought it necessary to give details of experiments in which such procedures were used.

Appendix

DETERMINATION OF SILVER IN TRADE EFFLUENTS

PRINCIPLE OF METHOD—

The silver will be accompanied by other metals in the effluent, and in the presence of chloride ions and organic materials it may be largely present in the form of complexes.

The silver, together with a number of other metals, is first extracted into a small volume of a concentrated solution of dithizone in carbon tetrachloride, whence it is removed selectively by treatment with an aqueous solution of ammonium thiocyanate. After destruction of this thiocyanate and re-solution of the silver in dilute nitric acid the final determination is made absorptiometrically.

RANGE—

For a 100-ml sample with a silver concentration of 0·2 to 20 μg per litre, a visual colour comparison or an absorptiometric procedure with micro-cells holding 0·5 to 1·0 ml was adopted. If the absorptiometer available has cells holding 4 to 7 ml, a correspondingly larger sample must be taken.

APPLICABILITY—

The method is of wide applicability. There is no interference by the presence, in each 100-ml sample, of 50 mg of organic material (tannin) or of 50 μg each of copper, ferric iron, lead and mercury, as well as the constituents normally present in this volume of tap-water.

APPARATUS—

Micro-separator—The micro-separator is shown in Fig. 2.

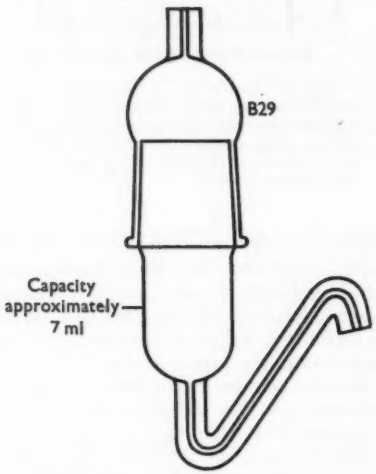


Fig. 2. Micro-separator

Pre-treatment of glassware—Soak all glassware first in hot chromic acid and then in diluted nitric acid (1 + 1); wash thoroughly with metal-free water. When all the surfaces are dry, wash those to be treated with a silicone water-repellent, *e.g.*, Repelcote (obtainable from Hopkin and Williams Ltd.), and dry in an oven.

REAGENTS—

Distilled water—Laboratory distilled water that has been passed through an ion-exchange column (*e.g.*, an Elgastat, type B 102, portable de-ioniser).

Sulphuric acid, concentrated—Analytical-reagent grade, sp.gr. 1·838 to 1·844.

Sulphuric acid, dilute, 0·5 N—Concentrated sulphuric acid diluted with distilled water.

Nitric acid, 2 N—Concentrated acid, sp.gr. 1·42 (laboratory-reagent grade), diluted with distilled water.

Carbon tetrachloride—Analytical-reagent grade 95 per cent., boiling between 76° and 78° C; for preparation of dithizone solution A.

For dithizone solution B, purify the carbon tetrachloride by allowing it to stand over bromine for 2 weeks. Then boil it under reflux with sodium hydroxide solution, shake with a solution of hydroxylamine hydrochloride, separate, and distil.

Dithizone solution A—A solution containing 100 mg of dithizone per litre, B.D.H. reagent, in carbon tetrachloride.

Dithizone solution B—A solution containing 4 mg of dithizone per litre, in carbon tetrachloride. The B.D.H. reagent is purified as described in the method for zinc in trade effluents (*Analyst*, 1957, **82**, 445), except that carbon tetrachloride is used as solvent instead of chloroform.

Ammonium thiocyanate solution—A 2 per cent. w/v solution in 1 per cent. sulphuric acid. Store this solution in a bottle containing 25 ml of dithizone - carbon tetrachloride solution.

Urea solution—A 10 per cent. w/v solution in distilled water. Store as for ammonium thiocyanate solution.

Hydroxylamine sulphate solution—A 20 per cent. w/v solution in distilled water. Store as for ammonium thiocyanate solution.

Standard silver solution—Dissolve 0·1574 g of silver nitrate (analytical-reagent grade) in 1 litre of 0·5 *N* sulphuric acid.

Immediately before use, dilute 10 ml of this solution to 1 litre.

$$1 \text{ ml} \equiv 1 \ \mu\text{g of silver.}$$

PROCEDURE—

Preliminary concentration of silver—

1. To each 100 ml of sample, contained in a 500-ml conical separating funnel, add 11 ml of concentrated sulphuric acid.

2. Extract the silver by shaking for 1 minute with 5 ml of dithizone solution A, collecting the extract in a 20-ml centrifuge tube.

3. Repeat the extraction twice more with 5-ml portions of dithizone solution A, combining the extracts in the centrifuge tube. Reject the aqueous phase.

NOTES—(*a*) In the presence of excessively large amounts of organic material, a scum may form at the interface between the two phases. This must be transferred with the organic phase.

(*b*) If the volume of sample is as great as 500 ml, a further two extractions with 5-ml portions of dithizone solution A should be undertaken, a second centrifuge tube being used.

4. Spin in a centrifuge, and remove the aqueous phase with a suction pipette. Add 2 ml of distilled water, spin, and again remove the aqueous phase. Transfer the solution of silver dithizonate in carbon tetrachloride to a 50-ml separating funnel.

Separation of silver—

5. Place 4 ml of ammonium thiocyanate solution in the centrifuge tube so as to collect any remaining droplets of organic phase and any scum; gently agitate the contents, and transfer quantitatively to the separating funnel. Stopper the funnel, shake the mixture for 1 minute, allow the phases to separate, and, with a suction pipette, transfer as much as possible of the aqueous phase to a 25-ml silica crucible.

6. Repeat stage 5 twice more. Run off and reject the organic phase from the separating funnel, and add the last few drops of the aqueous phase to the contents of the silica crucible.

7. Add 1·5 ml of concentrated sulphuric acid, evaporate under an infra-red lamp (see Note) and then to dryness with radiant heat from below as well as above the crucible. Add 0·3 ml of 2 *N* nitric acid, and warm until any solid residue is completely dissolved. Add 1 ml of urea solution and 1 ml of hydroxylamine sulphate solution, and digest the solution for 5 minutes near the boiling-point under the infra-red lamp. Cover the crucible with a watch-glass, and allow to cool to room temperature.

NOTE—Heating from above from a silica infra-red heater minimises "creeping" and is recommended. If such a heater is not available, heating from below on a hot-plate should be at as low a temperature as possible to avoid bumping. (It has been suggested that the use of an infra-red lamp in a metal casing might cause contamination from corrosion of the casing by the sulphuric acid vapours.)

Determination of silver—

8. Transfer the contents of the silica crucible to the micro-separator by means of a suction pipette, rinsing the crucible twice with 2-ml portions of 0·5 *N* sulphuric acid.

9. Add 1 ml of dithizone solution B, and mix with the aqueous phase by passing for 2 minutes a stream of nitrogen pre-saturated by passage through a solution of dithizone in carbon tetrachloride.

If the organic phase has a greenish hue, the amount of silver can be estimated as less than 1·5 μg. When this is so, carry out the determination according to Method A or B below.

If the organic phase is a clear yellow (showing that there is no excess of dithizone), proceed as described under "Procedure for Large Quantities of Silver."

Method A: Direct visual comparison

Prepare standards by placing in each of nine micro test-tubes (ignition tubes), 7½ cm × 1 cm, 1 ml of dithizone solution B and then 0·0, 0·2, 0·4 . . . 1·6 ml of the standard silver solution and 3·0, 2·8, 2·6 . . . 1·6 ml of 0·5 *N* sulphuric acid.

Extract the silver by agitation of the organic and aqueous phases together for 2 minutes, with the aid of a thin glass rod flattened at the bottom, beginning with the solution poorest in silver. By applying pressure at the top, transfer the mixed-colour organic phase from the micro-separator to a tenth test-tube, and wash it with 3 to 4 ml of the aqueous phase. Compare the sample and the standards, and estimate the silver content to the nearest 0·1 μg.

Direct sunlight must be avoided.

Method B: Absorptiometry with use of micro-cells

After equilibrating the aqueous and organic phases in the micro-separator, transfer the mixed-colour carbon tetrachloride phase to a micro-cell, and replace the lid. Measure the absorbancy in a Spekker absorptiometer, with use of an Ilford orange filter No. 607, or in a Beckman or Unicam spectrophotometer at $\lambda_{max.} = 620$ mμ against a comparison cell filled with dithizone solution B. Prepare a standard curve by adding a known amount of silver in the range 0·2 to 1·5 μg to 0·3 ml of 2 *N* nitric acid, 1 ml of the urea solution and 1 ml of hydroxylamine sulphate solution, and, after the addition of 1 ml of dithizone solution B, carry out the entire extraction process from stage 9.

Subtract the blank value obtained by carrying 100 ml of distilled water through the entire process from stage 1 to the final determination.

PROCEDURE FOR LARGE QUANTITIES OF SILVER—

If the organic phase in stage 4 is a clear yellow (showing that there is no excess of dithizone) add further 1-ml portions of the dilute dithizone solution B, and repeat the equilibration until a mixed colour is observed. Note the total volume "X" of the dithizone solution used.

The concentration of silver can then be determined by the visual method (Method A) on an absorptiometer (Method B) or by using an absorptiometer with micro-cell if the volume of the organic phase is sufficient.

In each instance the number of micrograms of silver is calculated by multiplying the figure obtained in this way by the factor "X."

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Determination of OO-Dimethyl S-(N-methylcarbamoylmethyl) Phosphorothiolothionate in Technical Rogor and its Formulations

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A liquid - liquid partition-chromatographic method is described for determining OO-dimethyl S-(N-methylcarbamoylmethyl) phosphorothiolothionate in insecticidal preparations containing Rogor. The eluted active ingredient can be determined spectrophotometrically as phosphovanadomolybdate or volumetrically by bromination.

The insecticide Rogor is now widely used commercially. It has both contact and systemic action, a wide spectrum of insecticidal activity and relatively low mammalian toxicity.

The technical chemical, when first introduced some years ago for experimental work, had a purity of about 70 per cent., but subsequent improvements in manufacturing processes have resulted in an increase in purity to over 90 per cent. The technical material may be formulated into emulsion concentrates (miscible oils), wettable powders and dusts. An analytical method was required for determining the content of the active ingredient, OO-dimethyl S-(N-methylcarbamolymethyl) phosphorothiolothionate, for which, as there is no accepted common name in the U.K., the term "dimethoate" will be used in this paper. Manufacturing impurities in technical Rogor may include OOS-trimethyl phosphorodithioate, OO-dimethyl phosphorodithioate, O-methyl S-(N-methylcarbamoylmethyl) phosphorothiolothionate and related compounds having a P=O group instead of P=S; thiopyrophosphates may also be present. The presence of these impurities makes it unlikely that a specific chemical test can be found for dimethoate.

A method depending on the acidic hydrolysis of dimethoate to monomethylamine has been described, but is not specific for dimethoate in Rogor.[1] Methods[2,3,4] have also been developed for determining dimethoate residues in crops, but these are not applicable to its determination in technical Rogor and its formulations.

It is known that the rate of alkaline hydrolysis of the active ingredient is more rapid than are those of most of the impurities. However, in the absence of complete knowledge of the identities of all the impurities present, this technique cannot be used with confidence.

From the nature of the probable impurities, it was thought that their partition coefficients between solvents and water would be sufficiently different from that of dimethoate to permit a separation to be achieved.

Most of the possible hydrolysis products of dimethoate that might be produced during manufacture or storage are likely to be more hydrophilic than is dimethoate itself. Oxidation products of dimethoate (containing P=O instead of P=S) are also likely to distribute more favourably into water from relatively non-polar solvents than is the active compound. Trimethyl phosphorodithioate was expected to have a higher partition coefficient between solvent and water than has dimethoate. After the work described in this paper had been completed, a paper was published[5] on the separation of bovine metabolites of radioactive dimethoate by gradient-elution partition chromatography on silica gel. This paper confirmed the behaviour predicted by us for some of the suspected impurities.

Experimental

Partition-chromatographic separation of dimethoate from impurities—

At the beginning of this work, the only known impurity present in fairly large amounts in the technical product was trimethyl phosphorodithioate. It was thought that if this compound could be separated from dimethoate by chromatography, the other likely impurities would also probably be separated.

A study of the partition coefficients of dimethoate and trimethyl phosphorodithioate between various pairs of solvents suggested that di*iso*propyl ether - light petroleum mixture and water would give a good separation of the two compounds. Initial experiments with kieselguhr - water columns and the ether - light petroleum mixture as eluting agent confirmed the separation and also showed that dimethyl phosphorodithioic acid preceded dimethoate. A typical chromatogram is shown in Fig. 1; with the column used, the dimethoate peak precedes those of the more hydrophilic impurities.

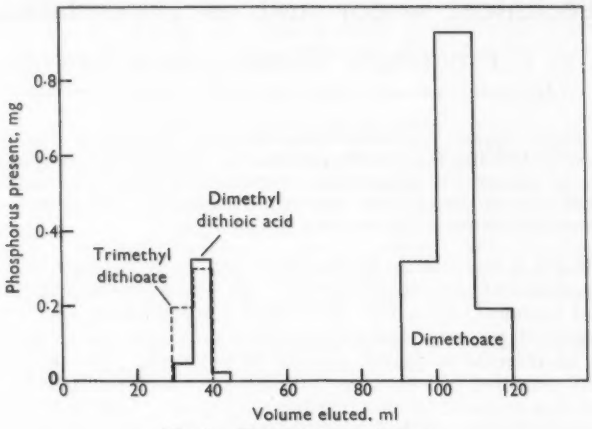


Fig. 1. Typical chromatogram

The measurement of dimethoate in the eluted fraction was carried out by spectrophotometric determination of phosphorus,[6] the procedure used being that described on p. 182. The analysis of pure dimethoate by partition chromatography gave values for purity between 98 and 100 per cent., and analyses of many samples of technical Rogor (expected purity 50 to 98 per cent.) gave values of the correct order. Analytical results are shown in Table I (see p. 183).

Verification of separation method—

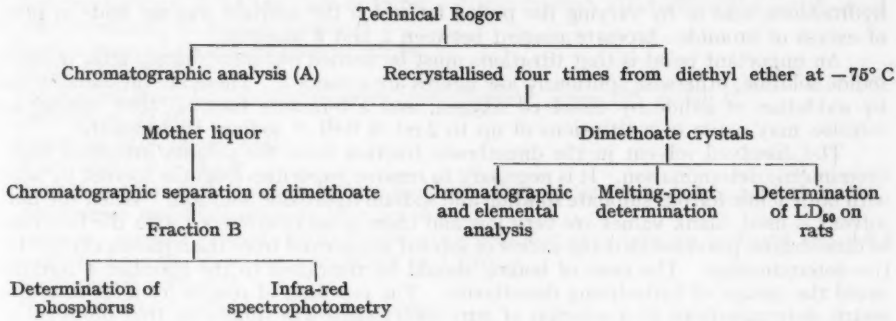
A method for isolating dimethoate having been established, it was necessary to confirm that the fraction taken for analysis contained only dimethoate and no significant amounts of interfering impurities.

Pure dimethoate can be prepared by multiple recrystallisation of the technical product, a concentration of impurities being simultaneously achieved. Technical Rogor was therefore divided into two fractions containing (*a*) impurities concentrate *plus* some dimethoate and (*b*) recrystallised dimethoate.

Fraction (*a*) was separated chromatographically as described above, and the dimethoate fraction was analysed chemically (by determining phosphorus) and by infra-red spectrophotometry.

Since infra-red spectrophotometry will probably not detect less than 1 to 2 per cent. of impurity in the dimethoate, other methods of identification had to be sought for recrystallised dimethoate. It has been shown[7] that Rogor produced by multiple recrystallisation has an acute oral LD_{50} to female rats of 680 mg per kg (95 per cent. confidence limits 618 to 748 mg per kg) and that this figure is depressed considerably by the presence of small amounts of certain hitherto-unidentified impurites. The LD_{50} is therefore an extremely sensitive measure of purity, and the purity of fraction (*b*) was checked toxicologically, as well as by sharpness of melting-point and elemental analysis.

A sample of technical Rogor containing approximately 72 per cent. of dimethoate was treated as shown by the diagram below—



The weight of crystals obtained *plus* that of the dimethoate found by chromatographic analysis of fraction B agreed closely with amount of dimethoate found in analysis A.

The dimethoate crystals had an LD_{50} of 672 mg per kg and melted sharply at 50° C. From present knowledge it is thought that this indicates a purity greater than 99 per cent. (Chromatography and elemental analysis indicated a purity of 99 per cent.)

The dimethoate fraction B from the mother liquor was analysed qualitatively and quantitatively for dimethoate by infra-red spectrophotometry. The purity was greater than 98 per cent., and the estimated content of dimethoate was within ± 3 per cent. of that found by determining phosphorus.

DETERMINATION OF DIMETHOATE IN FRACTION FROM PARTITION CHROMATOGRAPHY—

The active-ingredient fraction comprised 50 ml of di*iso*propyl ether - light petroleum mixture containing dimethoate. It was shown that the dimethoate could be quantitatively extracted into water by washing the solvent five times with 25-ml portions of water; this technique was used in most of the development work on the method. The dimethoate was converted to orthophosphate by treatment with perchloric acid, and the orthophosphate was determined spectrophotometrically by the phosphovanadomolybdate method. It was found that aqueous extraction was more rapid than direct evaporation of the organic solvent, because of difficulties with "bumping" when the latter procedure was used. The determination is described under "Procedure for Determining Dimethoate as Total Phosphorus," p. 182. Results for a series of sixteen determinations of phosphorus on a solution of pure dimethoate had a standard deviation equivalent to approximately $\pm 1{\cdot}3$ per cent.

The determination of phosphorus was somewhat lengthy, and, in particular, it was desirable to avoid the evaporation stage. Attempts were therefore made to convert dimethoate to orthophosphate without evaporation by using various oxidants, such as bromine, ceric ions and hypochlorite. None of the reagents tried gave quantitative conversion to orthophosphate at the dilution involved (5 mg per 100 to 150 ml).

A volumetric method is the most desirable from the point of view of speed. Alkaline hydrolysis is not satisfactory, as the small amount of dimethoate to be determined gives a

small titre of 0·01 *N* alkali; further, at the high dilution involved, a long period of hydrolysis at a high temperature is needed.

Iodine reacts with the alkaline hydrolysis products of dimethoate, but difficulty was encountered in standardising conditions so that a constant number of equivalents of iodine was consumed.

Dimethoate consumes 17 to 19 equivalents of ceric ion in approximately 2·5 *N* perchloric acid solution, but again suitable conditions in which the "ceric equivalent" of dimethoate was independent of the weight taken could not be found.

Bromination was found to give constant results over a wide range of conditions, the dimethoate consuming 14 equivalents of bromine. A direct titration was found to give low results, so work was concentrated on a back-titration technique. It was shown that the results found when 1- to 5-mg amounts of dimethoate were determined as described under "Procedure for Bromimetric Determination of Dimethoate in Chromatographic Fractions," p. 182, were not significantly affected by varying the acidity between 0·9 and 2·0 *N* in hydrochloric acid or by varying the period for which the solution was set aside in presence of excess of bromide - bromate reagent between 2 and 6 minutes.

An important point is that titrations must be carried out immediately after addition of iodide solution, otherwise spuriously low figures are obtained. These are presumably caused by oxidation of iodide by dissolved oxygen, and a 5-minute interval after adding iodide solution may cause over-titrations of up to 2 ml of 0·01 *N* sodium thiosulphate.

The dissolved solvent in the dimethoate fraction from the column interferes with the bromimetric determination. It is necessary to remove impurities from the solvent by washing with both acidic ferrous sulphate solution and sodium hydroxide solution. When the purified solvent is used, blank values are very low and there is no interference with the bromination of dimethoate, provided that the excess of solvent is removed from the aqueous extract before the determination. The time of boiling should be restricted to the specified 4 minutes to avoid the danger of hydrolysing dimethoate. The precision of results for a series of bromimetric determinations of a solution of pure dimethoate was similar to that obtained when the phosphorus method was used.

Method

If high-purity technical Rogor is to be analysed, the sample is dissolved directly in diethyl ether or the mixed solvent, and an aliquot is placed on the chromatographic column, see "Treatment of Sample," section (*i*). However, technical material containing less than about 90 per cent. of dimethoate may not be completely soluble in diethyl ether or the mixed solvent. Direct solution may then cause low results, presumably owing to partition of dimethoate from the solvent into the insoluble impurities. For such material, the chloroform extraction described under "Treatment of Sample," section (*ii*), must be used. This technique results in complete extraction of dimethoate into chloroform, with no material insoluble in either chloroform or water.

Most miscible-oil formulations containing Rogor can be dealt with by direct solution in ether before an aliquot is placed on the column, but, for some formulations, emulsifying or other formulating agents may be in part precipitated. This difficulty can sometimes be overcome by adding a little methanol to the ether solution. When the formulation does not respond to this treatment it may be necessary to carry out an extraction with light petroleum and methanol - water mixture. The amount of water used must be carefully controlled in order to avoid loss of dimethoate and emulsification during extraction. The conditions described under "Treatment of Sample," section (*iii*), were found by experiment to be optimal.

The direct-solution and light petroleum - methanol extraction procedures are satisfactory when the final determination is as total phosphorus; with certain formulations, however, spurious results are obtained when the bromimetric procedure is used.

Wettable powders and dusts containing Rogor presented some rather unexpected difficulties. With certain formulations, extraction with chloroform (the most favourable solvent for dimethoate) in a Soxhlet apparatus for 2 to 3 hours gives low results, owing to inefficient extraction and also, apparently, to decomposition of dimethoate in the boiling flask. Results are better when methylene chloride is used, but are still slightly low. Cold extraction with a suitable solvent, such as chloroform, and then centrifugation or filtration and washing are necessary to obtain quantitative results. With some dusts extraction in a Soxhlet apparatus for 6 hours with methylene chloride is satisfactory.

APPARATUS—

The chromatographic column consists of a glass tube 14 mm internal diameter and 40 cm long, constricted to 5 mm internal diameter at its lower end and fitted with a B19 ground-glass joint at its upper end. A 250-ml solvent reservoir is fitted with a B19 joint to connect with the column joint.

REAGENTS—

Unless otherwise stated, all materials should be of analytical-reagent grade.

Kieselguhr—Hyflo Super-Cel (obtainable from Johns-Manville Ltd., Artillery Row, London, S.W.1).

Mixed solvent—Mix equal volumes of technical grade di*iso*propyl ether and laboratory-reagent grade light petroleum, boiling range 60° to 80° C. Wash 2 litres of the mixture successively in a separating funnel with 100 ml of 2 *N* sodium hydroxide, two 50-ml portions of water, 100 ml of a 2 per cent. w/v solution of ferrous sulphate heptahydrate in *N* sulphuric acid and two further 50-ml portions of water. Filter through ether-extracted cotton-wool. This solvent should be freshly prepared.

Diethyl ether—Laboratory-reagent grade.

Methanol, industrial.

Light petroleum—Laboratory-reagent grade, boiling range 60° to 80° C.

Chloroform, B.P.

Perchloric acid, 60 per cent.

Nitric acid, sp.gr. 1·42.

Ammonium vanadate solution, 2·50 g per litre—Prepare in dilute nitric acid (1 + 50).

Ammonium molybdate solution, 50 g per litre.

Bromate - bromide reagent, 0·025 N—Dissolve 0·6959 g of potassium bromate and 4·0 g of potassium bromide in water, and dilute to 1 litre.

Hydrochloric acid, 6 N.

Potassium iodide solution, 100 g per litre.

Sodium thiosulphate, 0·01 N—Prepare from aged 0·1 *N* sodium thiosulphate by dilution with freshly boiled distilled water.

Starch solution, 10 g per litre.

PREPARATION OF COLUMN—

Weigh 20 g of Hyflo Super-Cel into a mortar, and, by pipette, add 10 ml of distilled water dropwise, with stirring. Triturate gently but thoroughly to homogenise the mixture, add sufficient mixed solvent to form a thin slurry, and mix well. Plug the bottom of the column with a small wad of ether-extracted cotton-wool, and pack the slurry into the column with a perforated disc as described by Martin. The length of a normal column is 25 to 30 cm. Wash the column with about 100 ml of mixed solvent, applying nitrogen pressure, at 2·5 to 3 ml per minute.

STANDARDISATION OF COLUMN—

Prepare a solution containing 10 g of dimethoate per litre in diethyl ether. Transfer 1 ml of this solution to the column from a 1-ml graduated pipette. By applying nitrogen pressure to the top of the column, force the solvent carefully through the column until its surface coincides with the surface of the packing. Carefully release the pressure, and wash the solution on to the column with two 1-ml portions of mixed solvent. Elute with mixed solvent at 2·5 to 3·0 ml per minute by applying nitrogen pressure to the top of the reservoir, and collect 10-ml fractions of the eluate. Transfer the fractions quantitatively to separate 50-ml Kjeldahl flasks, add 5 to 7 ml of water to each fraction, evaporate the organic layer on a water bath, and remove the last traces with a current of air from a hand bulb. Determine the phosphorus present as described under "Procedure for Determining Dimethoate as Total Phosphorus," p. 182. From an average column, the dimethoate is eluted in the tenth, eleventh and twelfth fractions.

TREATMENT OF SAMPLE—

(*i*) *For technical Rogor and miscible-oil formulations completely soluble in ether*—Weigh sufficient sample to contain about 0·5 g of dimethoate (0·25 g for bromimetric finish), and dissolve in diethyl ether. Make up to 50 ml in a calibrated flask. By pipette, place 1 ml

of the solution on the column, and wash it in with two 1-ml portions of mixed solvent as described above. Elute with mixed solvent at 2·5 to 3·0 ml per minute. Collect the 50-ml fraction determined by the standardisation to contain all the dimethoate and a 10-ml fraction on either side of the 50-ml fraction.

Determine the phosphorus in the 10-ml fractions as described under "Standardisation of Column" and "Procedure for Determining Dimethoate as Total Phosphorus."

Transfer the 50-ml fraction to a separating funnel, extract with five 25-ml portions of water, combine the aqueous layers, and evaporate over a burner to between 5 and 10 ml. Transfer quantitatively to a 50-ml Kjeldahl flask, and determine the dimethoate present as total phosphorus. Alternatively, determine dimethoate in the 50-ml fraction bromimetrically (see "Procedure for Bromimetric Determination of Dimethoate in Chromatographic Fractions"). Whichever method of determination is used, blank values should be determined for the complete procedure.

(*ii*) *For technical Rogor samples not completely soluble in ether*—In a separating funnel containing 20 ml of water and 7 ml of chloroform place sufficient sample to contain about 0·5 g of dimethoate (0·25 g for bromimetric finish), shake well, and allow to separate. Transfer the chloroform layer to another separating funnel, and wash with 7 ml of water. Extract the original 20 ml of aqueous extract with three 7-ml portions of chloroform, and wash each extract successively with the original 7-ml portion of water. Combine all chloroform extracts, evaporate to between 2 and 3 ml on a water bath, and remove as much as possible of the remaining solvent with a current of air. Dissolve the residue in ether, dilute to 50 ml, transfer 1 ml of the solution to the column, and continue as described in section (*i*).

(*iii*) *For certain Rogor liquid formulations containing interfering emulsifying agents*—Shake a mixture of 100 ml of methanol, 5 ml of water and 145 ml of light petroleum, and allow to separate. (The lower methanolic layer is solvent A and the upper layer is solvent B.)

In a separating funnel containing 20 ml of solvent B and 7 ml of solvent A place sufficient sample to contain about 0·5 g of dimethoate (0·25 g for bromimetric finish). Shake well, allow the layers to separate, and run the lower layer into a 100-ml flask. Extract with three 7-ml portions of solvent A, and combine all lower layers. Evaporate to between 1 and 5 ml on a water bath, dissolve the residue in ether, and dilute to 47 ml. Clarify the solution, if necessary, by dropwise addition of methanol, and dilute to 50 ml. Transfer 1 ml of solution to the column, and continue as described in section (*i*).

(*iv*) *For wettable-powder and dust formulations containing Rogor*—Extract a suitable weight of sample by stirring with excess of cold chloroform for 1 hour. Spin in a centrifuge, and decant the chloroform extract. Repeat the extraction (one or more times according to the type of filler), centrifugation and decantation, and combine the chloroform extracts. Evaporate to between 2 and 3 ml under reduced pressure, and continue as described in section (*iii*).

PROCEDURE FOR DETERMINING DIMETHOATE AS TOTAL PHOSPHORUS—

To the contents of the Kjeldahl flask add 4 ml of perchloric acid and 1 ml of nitric acid. Evaporate until fumes of perchloric acid are evolved, and heat gently, allowing perchloric acid to reflux in the neck of the flask, for 3 to 5 minutes. Cool, add 10 ml of water, and boil gently for about 5 minutes. Cool, dilute with water to about 35 ml in a calibrated flask, and add 5 ml of ammonium vanadate solution. Swirl the flask, add 5 ml of ammonium molybdate solution, dilute to 50 ml with water, and mix. After 30 to 40 minutes, measure the optical density against water in a 1-cm cell at 470 mμ, and read the equivalent amount of phosphorus from a graph prepared from the results obtained by using pure potassium dihydrogen orthophosphate. After allowance for the appropriate blank value, calculate the dimethoate content of the sample from the expression—

$$\text{Dimethoate content, \% w/w} = \frac{\text{Amount of phosphorus found, mg} \times 37}{\text{Weight of sample, g}}.$$

PROCEDURE FOR BROMIMETRIC DETERMINATION OF DIMETHOATE IN CHROMATOGRAPHIC FRACTIONS—

Transfer the 50-ml fraction of eluate containing dimethoate to a separating funnel, and extract with five 20-ml portions of water. Combine the extracts in a 250-ml iodine flask, heat rapidly to boiling-point, and boil for 4 minutes. Cool quickly to room temperature, and add 20 ml of 0·025 *N* bromate - bromide reagent and 40 ml of 6 *N* hydrochloric acid.

Mix well, set aside for 4·0 minutes, and carefully add 5 ml of potassium iodide solution through the stopper annulus. Titrate immediately against 0·01 *N* sodium thiosulphate with starch solution as indicator. Carry out a blank determination on a "clear" 50-ml fraction of eluted solvent. Calculate the dimethoate content of the sample from the expression—

$$\text{Dimethoate content, \% w/w} = \frac{0{\cdot}818\ (T_1 - T_2)}{\text{Weight of sample, g}},$$

in which T_1 and T_2 are the titres (in millilitres) obtained in the blank and sample determinations, respectively.

Note that certain formulants used in Rogor preparations interfere with the bromimetric determination. If such formulants are present, the dimethoate should be determined as total phosphorus. It is recommended that the bromimetric method should be used only for technical Rogor or Rogor formulations previously shown to be free from interfering ingredients.

Results

Many samples of technical Rogor having different degrees of purity and of Rogor formulations have been analysed by the proposed method, the dimethoate contents being determined both bromimetrically and as total phosphorus; some results for samples of technical Rogor are shown in Table I.

Table I

Dimethoate contents of samples of technical Rogor

Sample No.	Dimethoate content found— as total phosphorus, %	bromimetrically, %
1	70·5, 71, 70·5 (70)	—
2	72·5, 72·5	72·5, 72
3	56·5, 55·5, 56·5, 56·0	—
4	52	51·5, 52
5	93, 94, 93·5, 92	—
6	88, 88·5	88, 88
7	87·5, 88	86, 87

Several types of prepared miscible formulations containing aromatic or aliphatic solvents have also been analysed. Typical results, the dimethoate contents being determined as phosphorus, were—

Dimethoate present, %	25·2		27·2
Dimethoate found, %	24·8	25·0	28·1

Discussion of the method

The most important part of the work described is the verification that the chromatographic fraction taken for the determination contains only dimethoate.

The dimethoate crystals obtained as described under "Verification of Separation Method" had a high LD_{50}, indicating the absence of small amounts of "potentiating" impurities. The absence of possible non-toxic impurities (which are likely to be more easily removed by recrystallisation) was confirmed by the sharp melting-point. The dimethoate fraction from partition chromatography of the impurities is unlikely to contain closely related compounds having the group  since these compounds would have different partition coefficients from that of dimethoate itself. Compounds having the group  or  are unlikely to interfere appreciably with the infra-red determination. With these facts in mind, the purity of the dimethoate fraction was reasonably estimated at being greater than 98 per cent.;

further, there was quantitative agreement between infra-red and total-phosphorus determinations on the fraction.

Determinations of dimethoate in fractions from several samples of technical Rogor both bromimetrically and as total phosphorus show close agreement between results by the two procedures. This agreement is further evidence that the fraction taken contains only dimethoate.

We thank D. M. Sanderson for the toxicological work, R. Howes for interpreting infra-red spectra and the directors of Fisons Pest Control Limited for permission to publish this paper.

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Received *September 24th*, 1959

The Determination of Dieldrin

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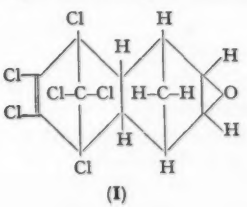
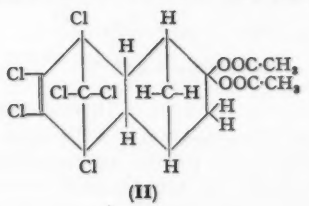
Small amounts of dieldrin are converted to the 2:4-dinitrophenylhydrazone of an isomeric ketone. The resulting colours, after intensification with alkali, are used as the basis for the determination of dieldrin deposits on special spray-target papers and also on mangold foliage.

After the development of a colorimetric method[1] for determining dieldrin, **I**, based on the use of a boron trifluoride reagent, alternative methods were sought that would avoid the use of this reagent, which was somewhat inconvenient to handle.

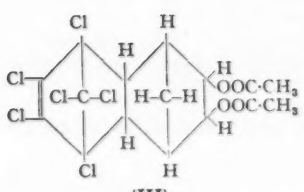
Experiments indicated that acetic anhydride in the presence of catalytic amounts of sulphuric acid yielded the *gem*-diacetate, **II**, instead of the *vic*-diacetate, **III**, that would



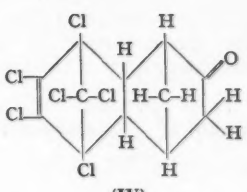
(I)



(II)



(III)



(IV)

be expected on the basis of similar acetylations catalysed by hydrogen ions.[2] The diacetate presumably resulted from a catalytic rearrangement of the epoxide ring to the ketone, **IV**,[3] and then an acetylation at the ketonic carbon atom, as described by Knoevenagel.[4] Hydrolysis

of the diacetate, **II**, would yield the ketone, **IV**, which was an intermediate in the previously developed colorimetric method.[1] In practice, it was unnecessary to utilise a separate hydrolysis stage before preparing a 2:4-dinitrophenylhydrazone, as the relatively slow hydrolysis catalysed by the sulphuric acid present in the 2:4-dinitrophenylhydrazine reagent solution is followed by the much faster 2:4-dinitrophenylhydrazone formation.

During the development of the method it became necessary to examine a number of spray-target papers. These are small (33 sq. cm) pieces of paper having a special coating[5] that prevents the spreading of spray droplets on impaction. When dyes are added to the spray liquid, such papers permit a visible assessment of spraying efficiency. In this instance the papers were used in the examination of spray formulations for the control of *Amblypelta cocophaga* in coconut palms.

Experimental

On the basis of experiments to be reported elsewhere, the acid-catalysed formation of the *gem*-diacetate was carried out by heating dieldrin with acetic anhydride containing 0·1 per cent. v/v of sulphuric acid for 30 minutes at 100° C. It was necessary to prepare the acetic anhydride - sulphuric acid mixture at 0° C to avoid a slight charring discoloration, which gave rise to higher blank values. Complete hydrolysis of the acetic anhydride was essential before isolation of the diacetate in order to avoid any possibility of acetic anhydride being carried forward into the preparation of the 2:4-dinitrophenylhydrazone. It was hoped that it would be unnecessary to isolate the diacetate before preparing the 2:4-dinitrophenylhydrazone. However, in acetic acid solution, the concentration of acetate ion was presumably too great to permit complete hydrolysis of the diacetate to the ketone before formation of the 2:4-dinitrophenylhydrazone. In a typical experiment only 40 per cent. of the 2:4-dinitrophenylhydrazone had been formed after 45 minutes at 60° C.

The simultaneous hydrolysis of the isolated diacetate and preparation of the 2:4-dinitrophenylhydrazone was carried out at 60° C, paper chromatography having indicated that the over-all rate of hydrazone formation was much more rapid at this temperature than at room temperature; a reaction time of 30 minutes was sufficient for the completion of the reaction. A standard graph was prepared, and the relationship between optical density and amount of dieldrin present was found to be $A = 3{\cdot}63 \times 10^{-3} B$, where A is the optical density after subtraction of the blank value, measured at 440 mμ[1] in a 1-cm cell, and B is the number of micrograms of dieldrin present. This expression indicates a slightly lower sensitivity than that obtained by using the boron trifluoride catalyst, presumably owing to side reactions.

When the method was applied to samples of the special spray-target papers, the surprisingly high blank value of 1·21 μg of "dieldrin" per sq. cm of paper was found. By using a chromatographic column of alumina conditioned to Brockmann activity II,[6] this interference was reduced to 0·18 μg per sq. cm of paper without significant loss of dieldrin.

Method

Reagents—

Benzene—Heat analytical-reagent grade benzene under reflux for 8 hours with 1 g each of trichloroacetic acid and 2:4-dinitrophenylhydrazine per litre, with use of a Dean and Stark trap. Fractionally distil, boil the distillate under reflux for 16 to 24 hours with sodium - potassium alloy, and re-fractionate.

Ethanol—Heat commercial absolute ethanol under reflux with 1 g of 2:4-dinitrophenylhydrazine and 0·3 ml of concentrated hydrochloric acid per litre for 8 hours. Fractionally distil through a Widmer column.

Acetic anhydride—Fractionally distil analytical-reagent grade acetic anhydride through a Widmer column, and discard the first 10 per cent. of the distillate.

Acetic anhydride reagent solution—Cool 10 ml of the acetic anhydride to between —5° and 0° C, and add 0·1 ml of sulphuric acid. Add 1 ml of the mixture to 9 ml of the acetic anhydride previously cooled to 0° C.

Acetic acid—Heat analytical-reagent grade acetic acid under reflux with 1 g of 2:4-dinitrophenylhydrazine per litre for 16 hours. Fractionally distil through a Widmer column.

Hydrolysis reagent solution—Slowly add 10 ml of concentrated sulphuric acid to 30 ml of water, cool, and add 60 ml of glacial acetic acid. Store this solution in a refrigerator.

2:4-*Dinitrophenylhydrazine reagent solution*—Dissolve 10 mg of analytical-reagent grade 2:4-dinitrophenylhydrazine that has been twice recrystallised from benzene in 5 ml of

20 per cent. v/v sulphuric acid. Prepare this solution freshly each day, and extract with 0·1 ml of benzene immediately before use.

Tetraethylammonium hydroxide solution, 25 per cent. w/v.

Hydrochloric acid, sp.gr. 1·18—Analytical-reagent grade.

Sodium hydroxide, 10 N.

Active carbon—Stir and boil 100 g of Darco G carbon (obtainable from the Darco Carbon Corporation, New York) with 200 ml of concentrated hydrochloric acid for 2 to 3 hours. Decant the acid, stir the carbon with two 500-ml portions of water, separate by filtration, and dry. Extract in a Soxhlet apparatus with glacial acetic acid for 3 hours, stir with two 500-ml portions of water, separate by filtration, and dry at 110° C.

PROCEDURE—

Wash the spray-target paper (approximately 33 sq. cm) in three separate beakers each containing 6 ml of benzene. Combine the washings, add 0·5 g each of calcium oxide and active carbon, and pass through a chromatographic column 15 mm in diameter containing 5 g of alumina conditioned to Brockmann activity II and covered by a layer of 5 g of anhydrous sodium sulphate. Wash the column with four 5-ml portions of benzene, combine the washings, and evaporate to dryness under reduced pressure in a water bath at 60° C. Add 1 ml of acetic anhydride reagent solution, and heat for 30 minutes in an oil-bath at 100° C. Cool, add 1 ml of hydrolysis reagent solution, and heat for a further 30 minutes at 100° C. Cool, and transfer to a separating funnel with 5 ml of benzene and 20 ml of water. Shake the mixture, discard the aqueous layer, and wash the benzene solution with 10 ml of 10 *N* sodium hydroxide and then with 20 ml of water. Dry the solution by filtration through a 2-cm layer of granular anhydrous sodium sulphate, wash the sodium sulphate with 10 ml of benzene, add the washings to the main solution, and evaporate to dryness. Dissolve the residue in 0·5 ml of ethanol, and add 0·1 ml of 2 : 4-dinitrophenylhydrazine reagent solution. Heat at 60° C for 30 minutes, transfer to a separating funnel with 5 ml of benzene, swirling the flask carefully for about 60 seconds, and wash the flask with a further 1 ml of benzene. Shake the benzene solution successively with 10 ml of concentrated hydrochloric acid, 5 ml of 10 *N* sodium hydroxide, 5 ml of concentrated hydrochloric acid and, finally, 20 ml of water. Dry the benzene layer by passing it through a 0·5-cm layer of granular anhydrous sodium sulphate into a stoppered graduated cylinder, and wash the sodium sulphate with benzene until the final volume is 7·5 ml. Add 2·5 ml of ethanol and 1 drop (approximately 0·05 ml) of tetraethylammonium hydroxide solution, mix thoroughly, and measure the absorption in a 1-cm cell at 440 mμ after 1 minute (but not longer than 10 minutes[1]). Interpolate the amount of dieldrin in the sample from the standard graph after subtraction of the optical density of a blank determination carried out in a similar manner.

RESULTS

Good recoveries were obtained when the proposed method was applied to samples prepared by dropping known volumes of a standard dieldrin solution on to spray-target papers and allowing the solvent to evaporate; the results were—

Dieldrin added, μg	..	..	10	25	50	75	100
Dieldrin found, μg	..	..	9·9	24·8	50·3	75·0	99·7

APPLICATION OF THE METHOD

When the method was applied to the determination of dieldrin on mangold leaves, the chromatographic separation of interfering plant constituents was unsatisfactory; blank values of 0·22 μg of "dieldrin" per sq. cm of leaf surface were encountered. Preliminary treatments with *p*-phenylhydrazine sulphonic acid, *p*-phenylhydrazine carboxylic acid, Girard P reagent, hydroxylamine or Linde molecular sieves failed to remove this interference, which was assumed to be caused by ketonic components of the leaf wax.

However, when the high blank value could be tolerated, chromatographic treatment of the extracts could be dispensed with. The results shown below indicate reasonable recoveries of dieldrin added to extracts of leaf material corresponding to 50 sq. cm of leaf surface—

Dieldrin added, μg	..	..	25	50	75
Dieldrin found, μg	..	..	28	48	70

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Received *October 26th*, 1959

The Determination of 1-Naphthyl Methylcarbamate (Sevin) Residues in Apples

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A procedure is described for determining 1-naphthyl methylcarbamate residues in apples. The carbamate is coupled with diazotised sulphanilamide to form a dye, which is then determined colorimetrically. Plant waxes are removed with acetonitrile and light petroleum, and interference from 1-naphthol (a breakdown product of 1-naphthyl methylcarbamate) and some naturally occurring phenolic compounds is overcome by preliminary extraction with 0·5 *N* sodium hydroxide. The optical density of the final solution is measured in a 1-cm cell at 520 mμ.

SEVIN (1-naphthyl methylcarbamate), a representative of a group of carbamates having insecticidal properties, appears to show promise in the control of certain pests,[1] notably, codling moth on apples. It is sparingly soluble in water, but fairly soluble in a wide range of organic solvents. Although stable in acid and neutral conditions, it is hydrolysed in alkaline media to 1-naphthol. It is stable to light and heat and has low mammalian toxicity, the insecticidal effect being exerted by cholinesterase inhibition.

Of the procedures so far used for determining Sevin residues, the enzymatic method[2] is non-specific, and the paper-chromatographic method,[3] used in the analysis of wine, was not suitable for our purpose. Chemical methods[3] depending on hydrolysis of the Sevin and subsequent determination of the liberated 1-naphthol with either aminoantipyrine or *p*-nitrobenzenediazonium fluoroborate suffer from interference by 1-naphthol present in the residue.

By coupling 1-naphthyl methylcarbamate with diazotised sulphanilamide, however, a red dye is produced without preliminary hydrolysis to 1-naphthol. Interference by 1-naphthol can be overcome by prior extraction of a solution of the sample in methylene chloride with 0·5 *N* sodium hydroxide, a treatment that also removes some of the naturally occurring phenols present in extracts of apples and so reduces the blank value.

To avoid turbidity in the colorimetric determinations, it was necessary to remove plant waxes by treating the extracts with acetonitrile. The traces of waxes soluble in acetonitrile were removed by adding a limited amount of water to the acetonitrile solution and then extracting with light petroleum. Subsequent addition of more water rendered the carbamate much less soluble, and it could be quantitatively extracted by methylene chloride. The coupling reaction must be carried out at about 3° C, otherwise blank values are high.

METHOD

REAGENTS—

Acetonitrile.

Light petroleum—The fraction boiling over the range 28° to 40° C.

Methylene chloride—Wash commercial-grade methylene chloride with water, and distil.

Sodium nitrite solution, 0·5 per cent. w/v, aqueous.

Sulphanilamide solution—Prepare a 0·5 per cent. solution of sulphanilamide in 2 *N* hydrochloric acid.

Sodium hydroxide, 4 and 0·5 N—Prepare from analytical-reagent grade material.
Ethanol, 96 per cent.
Ethanol, 50 per cent., aqueous.

PROCEDURE—

Cut 1000 g of the sample of apples into pieces, place in an Erlenmeyer flask, and cover with 1 litre of methylene chloride. Set the flask aside overnight, and then decant and filter the liquid. Place a 100-ml aliquot of the filtrate in a 150-ml beaker, and heat on a water bath to evaporate most of the solvent. Remove the last few millilitres of solvent by means of a current of air, add 5 ml of acetonitrile to the residue, and heat the mixture to boiling-point to dissolve as much of the plant waxes as possible. Allow to cool in a refrigerator, and then separate the insoluble waxy material by filtering the mixture through a cotton-wool plug into a 60-ml separating funnel. Wash the beaker and cotton-wool plug with cold acetonitrile until 10 ml of filtrate are obtained. Add 10 ml of water, and extract three times with 5-ml portions of light petroleum. After each extraction, withdraw the upper light petroleum layer by suction, and discard it. Dilute the acetonitrile - water mixture with 20 ml of water, and extract three times with 10-ml portions of methylene chloride. Wash the combined methylene chloride extracts with a 5-ml and then a 2-ml portion of 0·5 *N* sodium hydroxide and finally with three 5-ml portions of water. Transfer the washed extract to a 50-ml calibrated flask, evaporate most of the solvent on a water bath, and remove the last traces by means of a current of air. Dissolve the residue in 15 ml of 96 per cent. ethanol, add 10 ml of water, cool in ice, and add 2 ml each of sodium nitrite and sulphanilamide solutions. Set aside for 10 minutes, add 2·5 ml of 4 *N* sodium hydroxide, and dilute to the mark with 50 per cent. aqueous ethanol. Set aside in a refrigerator for at least 3 hours, and then measure the optical density of the solution in a 1-cm cell at 520 mμ.

PREPARATION OF CALIBRATION GRAPH—

Prepare an ethanolic solution containing 100 μg of 1-naphthyl methylcarbamate (melting-point 141° to 142° C) per ml. Treat portions of this solution as described under "Procedure," and plot a graph of optical density against concentration of carbamate present. The graph should be a straight line passing through the origin.

RESULTS

Recoveries by the proposed method were determined by analysing apple extracts to which known amounts of 1-naphthyl methylcarbamate and 1-naphthol had been added. The results are shown in Table I, from which it can be seen that the average recovery was 96 per cent. Corrections were made for the average optical density in absence of added carbamate; this value was 0·025, which is equivalent to 7 μg of 1-naphthyl methylcarbamate.

TABLE I

RECOVERY OF 1-NAPHTHYL METHYLCARBAMATE ADDED TO EXTRACTS OF APPLES

1-Naphthyl methylcarbamate added, μg	1-Naphthol added, μg	Recovery of 1-naphthyl methylcarbamate	
		μg	%
0	150	0	—
50	—	49	98
75	250	73	97
100	—	98	98
100	250	96	96
125	350	116	93
150	—	143	95
150	—	141	94
200	—	190	95

Samples of Goud Rennette apples were analysed by the proposed method at intervals after having been sprayed with Sevin. The results, from which the "half-life" of Sevin was calculated to be 5·2 days, are shown in Table II.

TABLE II

CONCENTRATIONS OF 1-NAPHTHYL METHYLCARBAMATE FOUND IN APPLES SPRAYED WITH SEVIN

Time after spraying, days	1-Naphthyl methylcarbamate found, p.p.m.
0	1·1, 1·1, 0·7, 1·1 (Mean 1·0)
4	0·9, 1·0, 0·6, 0·8 (Mean 0·8)
10	0·3, 0·3, 0·2, 0·3 (Mean 0·3)

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Received *September 17th*, 1959

The Determination of Digestible Carbohydrates in Poultry Foods

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A simple method is described for the determination of sugar *plus* starch ("available carbohydrate") expressed as a percentage of starch. It is shown that the expression "available carbohydrate *plus* 4·9" affords a reasonable measure of the digestible carbohydrate in individual and compounded foods for growing and adult fowls. For young chicks, 2·5 would be a better factor than 4·9.

THE carbohydrates in animal foods are divided into crude fibre and nitrogen-free extractives, a partition based on digestibility trials with oxen,[1] in which it was found that the crude fibre was roughly equal to the indigestible carbohydrate and the nitrogen-free extractives to the digestible carbohydrate.

It is well known that the fowl has not the digestive ability of the ruminant, and hence it follows that the crude fibre - nitrogen-free extractives partition is not applicable to poultry.

Accordingly, the digestibilities of more chemically defined components of the carbohydrate complex—sugar, dextrin *plus* starch, pentosan, cellulose and lignin[2,3,4,5,6]—were determined. It was found that sugar and dextrin *plus* starch were completely digested, that cellulose and lignin were indigestible and that, although some pentosan was digested, this only became important in a few foods, notably the wheat offals.

In human nutrition the sum of the sugars multiplied by 0·91 and added to the starch is termed the available carbohydrate. The same nomenclature was adopted for the parameter in poultry foods. The available-carbohydrate contents of eleven foods and four compounded diets were determined, and at the same time the digestible-carbohydrate contents were estimated by digestibility trials. Statistical analysis of the results showed that there was a highly significant correlation between the contents of available and digestible carbohydrates ($r = +0{\cdot}989$) and that the regression equation was—

$$\text{Digestible carbohydrate} = \text{available carbohydrate} + 4{\cdot}9.^{7}$$

In these trials the sugars and starches were determined separately by a macro modification of McCance, Widdowson and Shackleton's method,[8] except that the mixture of glucose and maltose resulting from the enzymic action was converted wholly to glucose by acid hydrolysis. The method took about 4 days to complete and was therefore obviously unsuitable as a routine for feedingstuffs analysis.

Re-examination of the method showed that it could be simplified considerably to give a value for the available carbohydrate only; the details are described below.

METHOD

A 1-g sample of the food is weighed into a 100-ml flask. Monax-glass flasks without lips and fitted with Oxoid metal caps are most suitable. The solid is moistened with a few drops of ethanol, about 20 ml of water are added, and, with continuous swirling, the contents of the flask are brought to the boiling-point over a naked flame to gelatinise the starches. After the flask has been allowed to cool, 0·5 ml of 5 per cent. v/v acetic acid and 0·1 to 0·2 g of takadiastase (obtainable from Parke, Davis and Co. Ltd.; standardised with talc) are added, the contents of the flask are mixed, and the walls are washed down with the minimum amount of water. A 0·5-ml portion of toluene is added, and the flasks, covered with metal caps, are kept at 37° C overnight.

TABLE I

COMPARISON OF AVAILABLE AND DIGESTIBLE CARBOHYDRATES IN REPLICATE MIXES OF THE SAME MASH FORMULA

No. of mix	Available carbohydrate +4·9, %	Digestible carbohydrate, %
1	38·1	38·2
2	40·1	39·4
3	40·3	40·0
4	41·3	41·8
5	41·5	42·1
6	40·5	43·6
7	40·8	39·4
8	42·4	40·5
9	40·6	39·4
10	41·6	39·6
11	41·1	42·0
12	42·4	40·1
Mean	40·9	40·4

TABLE II

COMPARISON OF DIGESTIBLE AND AVAILABLE CARBOHYDRATES IN DIFFERENT FORMULAE

	Digestible carbohydrate, %	Available carbohydrate, %
Chick mashes—		
A (14 to 21 days)	35·0	33·1
A (35 to 42 days)	35·5	33·1
B (25 to 28 days)	36·4	33·9
B (68 days)	38·1	33·9
C (0 to 5 weeks)	37·4	38·4
E (0 to 5 weeks)	38·9	38·7
D (0 to 9 weeks)	43·4	39·4
Chick mashes supplemented with fat—		
F (10 per cent. of beef dripping included) (0 to 10 weeks)	29·5	30·4
G (5·4 per cent. of fat included*) (0 to 5 weeks)	33·2	34·6
H (10·8 per cent. of fat included*) (0 to 5 weeks)	24·7	28·8
Growers' mash—		
J (10 weeks)	42·6	39·1
Layers' mashes—		
K	31·8	25·2
L	43·3	38·5

* Mixture of equal parts of beef dripping and olive oil.

The incubated contents are heated to boiling and filtered hot through a Whatman No. 3 filter-paper in a Buchner funnel, and the residue is washed twice with boiling water. The filtrate is made up to 190 ml, and clarified by the addition of 5 ml of 5 per cent. w/v zinc sulphate solution and then of 5 ml of 3·67 per cent. w/v potassium ferrocyanide solution. The suspension is filtered through a 15-cm Whatman No. 1 filter-paper. One-hundred millilitres of the filtrate in a 250-ml Monax-glass flask are made approximately 1·5 *N* by adding 6 ml of 72 per cent. w/w sulphuric acid, and the flask is covered with a metal cap and heated in steam for 2 hours. (A fish kettle with the floor raised 3 to 3·5 cm and heated by a double gas-ring

TABLE III

COMPOSITION OF SOME COMPOUNDED DIETS AND POULTRY FOODS

No.		Moisture, %	Protein, %	Oil, %	Total carbohydrate, %	Nitrogen-free extractives, %	Available carbohydrate, %	Ash, %
A.	*Compounded diets*—							
1.	Chick mash*	12·7	19·7	4·5	56·6	52·8	37·4	6·5
2.	Chick crumbs*	11·6	22·7	3·5	56·0	52·6	39·9	6·2
3.	Growers*	12·8	19·3	4·2	57·4	54·2	43·7	6·3
4.	Growers*	13·3	14·4	3·9	63·3	56·4	37·1	5·1
5.	Layers*	13·3	15·4	3·8	62·3	55·8	37·2	5·2
6.	PRC chick	11·6	18·2	7·8	56·5	51·9	36·6	5·9
7.	PRC breeder	12·5	15·1	5·9	60·8	56·1	38·6	5·7
8.	Breeders' mash*	11·8	18·4	3·6	59·8	54·0	34·2	6·4
9.	High-energy layers' mash*	11·8	16·0	3·5	60·3	56·0	37·8	8·4
B.	*Cereals and cereal by-products*—							
10.	Barley (Scotch)	16·0	7·8	1·5	72·4	68·5	53·9	2·3
11.	Barley (Canadian)	12·6	11·8	2·0	71·6	68·2	51·4	2·0
12.	Maize (Yugoslavian)	14·7	8·1	4·0	72·1	69·9	52·0	1·1
13.	Maize (Plate)	12·8	9·3	4·2	72·2	70·7	53·2	1·5
14.	Maize (Egyptian)	11·5	6·7	4·7	75·9	73·7	53·0	1·2
15.	Maize (U.S.A.)	14·5	8·2	4·4	71·5	69·5	54·1	1·4
16.	Maize germ (expeller)	8·3	20·8	11·0	58·3	44·4	12·9	1·6
17.	Maize gluten feed	11·2	22·6	7·0	53·4	47·0	15·3	5·8
18.	Maize gluten meal	10·6	40·4	4·7	40·2	36·0	14·5	4·1
19.	Milo	13·9	9·7	2·8	72·2	70·3	53·6	1·4
20.	Oats (Scotch)	14·3	8·2	5·7	67·1	58·9	47·7	4·7
21.	Oats (Plate)	11·6	10·5	6·5	67·7	56·1	38·4	3·7
22.	Groats	12·8	10·6	5·8	68·8	66·2	53·9	2·0
23.	Wheat (Scotch)	15·9	8·6	1·5	72·3	70·3	63·2	1·6
24.	Wheat (Irish)	13·3	12·6	1·9	70·9	68·0	53·7	1·3
25.	Wheat (Italian)	12·9	11·7	1·5	72·7	70·9	58·0	1·2
26.	Wheat (U.S.A.)	13·7	10·8	1·6	72·6	70·3	58·5	1·3
27.	Wheat bran	14·2	15·7	4·2	61·1	51·8	22·9	4·8
28.	Wheat parings	13·8	16·5	4·3	62·9	60·5	50·8	2·5
29.	Wheat superfine wheatfeed	12·8	12·7	3·7	68·4	63·8	48·9	2·4
30.	Wheat germ (expeller)	11·1	24·8	7·3	52·5	49·6	30·0	4·3
C.	*Vegetable proteins*—							
31.	Bean meal	15·0	25·3	0·9	56·0	49·5	27·2	2·8
32.	Cottonseed (expeller)	9·9	37·8	6·1	39·5	30·9	8·6	6·7
33.	Groundnut (expeller)	8·0	49·5	5·3	31·4	26·7	12·8	5·8
34.	Groundnut (extracted)	10·3	44·6	1·8	37·2	22·0	8·8	6·1
35.	Linseed (expeller) (Canadian)	11·0	34·1	4·8	44·6	35·5	9·4	5·5
36.	Linseed (expeller)	11·2	34·1	6·3	43·1	35·0	5·3	5·3
37.	Pea meal	12·9	27·1	1·7	5·55	49·1	23·2	2·8
38.	Sesame (expeller)	9·5	38·0	8·4	31·4	27·1	3·3	12·7
39.	Soya (expeller)	11·6	46·5	4·4	31·7	26·1	8·2	5·8
40.	Soya (extracted)	12·0	44·1	0·8	37·7	32·2	11·1	5·4
41.	Sunflower (extracted)	10·7	35·6	2·8	44·5	30·4	8·1	6·4
D.	*Miscellaneous*—							
42.	Distillers' dried solubles	5·8	23·4	0·5	46·3	46·3	9·6	24·0
43.	Grass meal (14%)	11·4	12·4	4·5	61·8	38·1	5·2	9·9
44.	Grass meal (17%)	7·6	13·3	4·9	64·0	45·3	5·9	10·2
45.	Grass meal (18%)	8·5	17·1	5·1	60·9	37·2	10·6	8·4
46.	Locust bean	13·1	3·7	1·5	80·5	75·9	44·5	1·7
47.	Milk (dried)	8·0	33·7	0·2	50·9	50·9	40·9	7·2
48.	Molasses	28·7	4·2	—	58·1	58·1	37·6	9·0
49.	Potato meal	8·7	8·7	0·2	79·2	79·2	60·2	3·2
50.	Seaweed meal	15·8	5·4	1·9	55·6	50·7	Trace	21·3
51.	Whale solubles	42·1	47·7	0·9	3·7	3·7	—	5·6
52.	Yeast, dried brewers'	9·4	41·7	9·4	31·6	31·6	13·0	7·9
53.	Grass meal, E. Lothian (17%)	9·9	16·1	4·0	62·2	41·7	9·3	7·8
54.	Grass meal, E. Lothian (18%)	9·9	13·5	4·6	63·8	44·8	9·3	8·2
55.	Lucerne meal (S. African)	11·3	14·5	2·7	64·2	35·9	5·0	7·3

* Sample provided by courtesy of a local provender miller.

makes a suitable steamer.) When the solution is cool, it is neutralised with about 14 ml of 40 per cent. w/v sodium hydroxide solution and dilute hydrochloric acid, the volume is recorded, and the sugar content is determined by titration with Fehling's solution, 1 per cent. methylene blue solution being used as indicator. For cereals and compounded diets 10 ml of Fehling's solution are taken and the glucose content of the sugar solution is determined with use of Lane and Eynon's Tables.[9] When dried grass or vegetable protein supplements are analysed, the resultant glucose content is too low to permit the use of 10 ml of Fehling's solution; 4 ml of Fehling's solution are therefore used, which are equivalent to 19 mg of glucose. In both instances, the percentage of glucose found $\times$ 0·91 is reported as the percentage of available carbohydrate.

During this work it was found that clarification with a barium hydroxide - zinc sulphate solution[10] was equally effective and did not introduce ions into the solution, but as treatment with ion-exchange resins[11] for the removal of acidic and basic amino acids did not affect the final result, the zinc sulphate - potassium ferrocyanide procedure was adopted to keep the method in line with that specified for sugars in the Fertiliser and Feeding Stuffs Regulations, 1955.[12]

Results

The relationship has been checked in two ways, by a comparison of the available- and digestible-carbohydrate contents of a series of consecutive mixes of the same mash formula (see Table I) and by a comparison of these in diets fed to birds of different ages (see Table II).

It can be seen that agreement between digestible carbohydrate and available carbohydrate *plus* 4·9 is close for adults and growers. For chicks, a constant of 2·5 would be better than 4·9 for diets not supplemented with fat. Fat-supplemented diets present new problems, which are under investigation.

Results for the more common poultry foods and some compounded diets are shown in Table III.

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First received *March 26th*, 1959
Amended, *October 19th*, 1959

A Method for Determining Non-ionic Surface-active Agents in Oils and Solvent Extracts from Wool

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The non-anionic surface-active agents are separated from fatty and mineral oils by passing an aqueous ethanolic dispersion of the sample through an alumina column and eluting with water. The non-ionic compound passes through the column, whereas fatty materials are retained. The non-ionic compound is determined in the eluate by precipitation with molybdophosphoric acid solution.

THE use of non-ionic surface-active agents has recently increased in the textile industries. Agents of this type are used as detergents and anti-static dressings for wool and man-made fibres, as emulsifying agents and as scouring assistants for mineral-based wool oils.[1] A recent development is the addition of a mixture of two such compounds to wool - Terylene blends to facilitate scouring.[2]

Several methods have been described for the determination in solution of non-ionic surface-active agents based on polyoxyethylene. Two of these methods—the molybdophosphoric acid method described by Oliver and Preston[3] and the colorimetric method described by Brown and Hayes[4]—have been used in these laboratories, but the presence of a substantial amount of fatty matter and dyes, as in the solvent extracts from wool, interferes with both methods and necessitates a preliminary separation. We have shown that, when an aqueous ethanolic dispersion of an oil and a non-ionic compound is passed through an alumina column, the fatty matter is retained, whereas the non-ionic agent passes through. This method was developed for determining the alkylated aryl ethers of polyoxyethylene containing different numbers of ethylene oxide units. Proprietary products of this type include Ethylan CP and BCP (Lankro Chemicals Ltd.), Nonidet P40 (Shell Chemicals Ltd.), Lissapol NX (Imperial Chemical Industries Ltd.) and Texofor F10 (Glovers Chemicals Ltd.). These products are soluble in water and substantially insoluble in neutral fatty oils and mineral oil, but can be solubilised in these oils with the help of oleic acid and water or polyoxyethylene derivatives containing a short glycol chain.

Method

APPARATUS—

Chromatographic tube—A glass tube, 60 cm × about 1·1 cm, constricted at one end (a 50-ml tap-less burette is suitable).

REAGENTS—

Aluminium oxide—Chromatographic grade, 100 to 200 mesh, Brockmann activity I. Before use, elute the alumina with water, ethanol and light petroleum (boiling below 40° C), and dry by drawing a current of dry air through it.

Ethanol, absolute.

Ethanol, 50 per cent., aqueous.

Diethyl ether, peroxide-free.

Hydrochloric acid, diluted (1 + 3).

Barium chloride solution, 10 per cent.

Molybdophosphoric acid solution, 10 per cent.

PROCEDURE—

Place a small plug of fat-free cotton-wool in the constricted part of the chromatographic tube, and cover with a ½-inch layer of Whatman No. 1 filter-paper macerated in water. Measure 10 ml of prepared alumina into a beaker, mix with water, and pour into the tube, maintaining a head of water above the alumina.

Weigh a suitable amount of oil or solvent extract from wool (containing 10 to 100 mg of non-ionic compound) into a 100-ml flask, add 5 ml of ethanol and then 5 ml of barium

chloride solution, and shake to disperse the sample (warm the flask if dispersion is difficult). When the meniscus of the water in the chromatographic tube has reached the surface of the alumina, pour the contents of the flask on to the column. Rinse the flask with three 3-ml portions of 50 per cent. aqueous ethanol, and pour the rinsings on to the column (see Note).

Place 100 ml of water in the flask, and, when the liquid level in the tube has reached the surface of the alumina, fill the tube with water from the flask. When all the water has been added, allow the column to drain dry.

As it is collected, filter the eluate through an 11-cm Whatman No. 42 filter-paper into a 250-ml beaker. When elution is complete, wash the jet of the tube with a little ethanol, and collect the ethanol on the filter-paper. Finally, wash the filter-paper with 30 ml of ethanol. To the contents of the beaker add 5 ml each of diluted hydrochloric acid, barium chloride solution and molybdophosphoric acid solution (in that order). Boil to coagulate the precipitate, set aside overnight, and then filter through a No. 4 sintered-glass crucible.

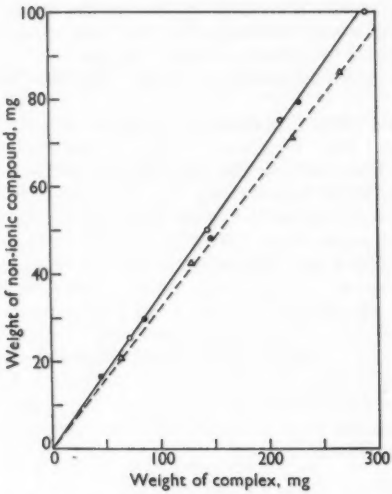

Fig. 1. Direct determination of non-ionic compounds with molybdophosphoric acid: △, Ethylan CP; ○, Lissapol NX; ●, Nonidet P40

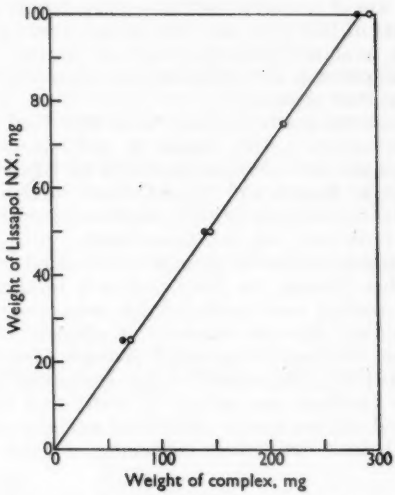

Fig. 2. Comparison of direct and chromatographic determinations: ○, direct; ●, after passage through column

Wash the precipitate with 100 ml of water and then sufficient ethanol to fill the crucible. Finally, fill the crucible with diethyl ether, and allow to drain. Dry the crucible to constant weight at 100° C.

NOTE—For solvent extracts from wool, it may be more convenient to proceed as follows. Pour 5 ml of barium chloride solution on to the column, disperse the sample in 10 ml of warm ethanol, pour the dispersion on to the column while still warm, and then pour a further 5-ml portion of barium chloride solution on to the column. Rinse the flask with three 3-ml portions of ethanol, and pour the rinsings on to the column, each portion of ethanol being preceded by 3 ml of water.

EXPRESSION OF RESULTS

Fig. 1 shows the calibration graphs obtained when known amounts of Ethylan CP, Lissapol NX and Nonidet P40 were determined directly by the molybdophosphoric acid method.[3] The results indicate only small differences between these products. When the non-ionic compound is known, therefore, the amount present in the oil can be calculated from a calibration graph obtained by direct determination of the compound itself. When the agent is not precisely known, it can be expressed in terms of a specific product, *e.g.*, as Lissapol NX or Ethylan CP. Alternatively, a composite graph based on Fig. 1 could be used.

Applications of the method

Recovery of Lissapol NX from the column—

The recovery of Lissapol NX was found by determining the amount of the agent eluted after a measured volume of an aqueous solution of Lissapol NX had been passed through the column and comparing it with the amount found by direct determination. The results are shown in Fig. 2 and indicate that recovery was complete.

Determinations in presence of oils—

Lissapol NX mixed with mineral oil—Lissapol NX is incompletely soluble in mineral oil. About 30 mg of the agent were mixed with about 300 mg of mineral oil (Pool 5D type), and the mixture was passed through the alumina column as described above. The results are shown in Table I; satisfactory recovery of the agent is indicated.

Lissapol NX dissolved in combing oil—Lissapol NX is soluble to the extent of 5 to 10 per cent. in proprietary castor - sperm type combing oils containing about 4·5 per cent. of free fatty acids. The surface-active agent dissolved in such a combing oil was recovered as described for Lissapol NX mixed with mineral oil. The results are also shown in Table I and indicate satisfactory recovery.

Nonidet P40 solubilised in mineral oil—The non-ionic surface-active agents being investigated, although incompletely soluble in mineral oil, can be solubilised by adding free fatty acid and water. In order to ascertain whether or not the surface-active agent could be recovered when completely solubilised, a mixture containing 10 per cent. each of Nonidet P40 and oleic acid, 2·5 per cent. of water and 77·5 per cent. of mineral oil was prepared, and the amounts of Nonidet P40 in samples of the mixture weighing from 0·18 to 0·85 g were determined. The results are shown in Table II and indicate slightly high recoveries of the surface-active agent. The mean recovery was 103·5 per cent. and the degree of error was of the order frequently found in oil analysis.

Determinations in solvent extracts of wool—

Green, Harker and Howitt[5] consider that the most effective solvent for the removal of fats, soap and other surface-active material from wool is an azeotropic mixture of benzene and methanol (3 + 2). It was therefore of interest to determine the recovery of surface-active agents present in such an extract.

Table I

Recovery of Lissapol NX from oils

Weight of oil present, mg	Weight of Lissapol NX present, mg	Weight of complex obtained, mg	Recovery	
			mg	%
Lissapol mixed with mineral oil—				
342·9	30·2	89·9	31·4	104·0
327·5	29·9	85·0	29·7	99·0
297·4	27·9	78·8	27·5	98·8
334·5	27·8	79·6	27·8	100·0
Lissapol dissolved in combing oil—				
290·6	33·6	94·6	33·0	98·4
300·0	31·4	86·4	30·4	97·4
332·3	30·6	86·2	30·2	98·7
327·3	28·6	79·5	27·8	97·1

Table II

Recovery of Nonidet P40 from blended mineral-based oil

Weight of Nonidet P40 present, mg	Weight of complex obtained, mg	Recovery	
		mg	%
18·7	60·5	19·9	106·6
32·5	102·7	33·6	103·4
36·8	115·6	37·8	102·2
50·9	162·4	53·2	104·6
61·0	191·4	62·7	102·7
70·2	221·3	72·7	103·6
84·6	262·7	85·8	101·6

TABLE III

RECOVERY OF ETHYLAN CP ADDED TO BENZENE - METHANOL EXTRACTS FROM WOOL

Sample	Weight of extract, mg	Weight of Ethylan CP added, mg	Weight of complex obtained, mg	Recovery	
				mg	%
Undyed wool top	533·6	19·2	63·1	20·3	105·8
	532·1	18·7	58·8	18·9	101·2
	509·8	19·0	62·3	20·1	105·8
Dyed wool top	500·0	28·9	90·1	29·1	100·4
	504·4	18·6	61·1	19·7	105·9
	448·6	20·4	64·4	20·7	101·6

Some 10-g samples of undyed wool top and top dyed black by an after-chrome process, each containing about 3·5 per cent. of a castor - sperm type combing oil, were extracted for 4 hours with benzene - methanol mixture in a Soxhlet extractor. After the extracts had been dried and weighed, about 20 mg of Ethylan CP were accurately weighed into each flask. In order to ensure that the non-ionic compound was completely mixed with the extract, about 5 ml of solvent were placed in each flask and the contents were again evaporated to dryness. The surface-active agent was then determined; the results are shown in Table III and indicate satisfactory recovery.

CONCLUSIONS

The results show that polyethylene glycol ethers containing about ten ethylene oxide units can be determined in fatty oils, mineral oils and solvent extracts from wool.

Other types of non-ionic compound differ chemically or physically from the type considered here, *e.g.*, alkyl or aryl alkyl ethers containing one to five ethylene oxide units. Such products are freely soluble in neutral and mineral oils, but only sparingly soluble in water. Polyethylene glycol esters of fatty acids can differ in chemical and physical properties from polyethylene glycol ethers. It is hoped to apply the proposed method to the determination of these types of non-ionic compounds.

We wish to thank Dr. F. F. Elsworth for much helpful advice.

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Received *September 22nd*, 1959

The Efficiency of Absorbers in Industrial Hygiene Air Analysis

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The principles involved in the use of liquid absorbers for air sampling in the analytical control of atmospheric contamination have been reviewed. The effects of the volume of air sampled, the rate of sampling and the design of the absorber on the efficiency of absorption have been studied by using test atmospheres containing ethylene oxide and chlorobenzene as examples of systems involving absorption by solution and by reaction.

MOST methods described for determining toxic substances in the atmosphere require a measured sample of air to be drawn through a liquid to extract the toxic substance, the liquid subsequently being analysed by a suitable quantitative procedure. A wide range of absorbing

equipment has been described for this purpose,[1] with little indication of how to choose between the various types. In order to develop a rational approach to the design and use of absorbers for air analysis, it is necessary to consider the theoretical principles involved in the extraction of a toxic substance from an air sample by passing it through a liquid.

If the substance in the atmosphere is a gas or vapour, it can be extracted either by solution in the absorbing liquid or by chemical reaction with the liquid or with some component therein. For particulate matter in air neither solution nor reaction is essential, as a particle wetted by the absorbing liquid is not likely to re-enter the gas phase. These three types of absorption will be considered separately.

RETENTION OF GASES AND VAPOURS BY SOLUTION—

The theory of the absorption of gases and vapours from air by solution in liquids was developed by Elkins, Hobby and Fuller.[2] These workers assumed that the vapour behaved as a perfect gas, that it dissolved to give a perfect solution and that, as it bubbled through the solvent, the concentration of the vapour in air reached equilibrium with the concentration in solution. Their equation, which has recently been re-established by Neale and Perry,[3] can be expressed more conveniently in the form—

$$E = v/VK\ (1 - e^{-VK/v})$$

where E is the efficiency of absorption for a volume V of air, *i.e.*, the fraction of the vapour in volume V retained by the liquid in a single absorber, v is the volume of absorbing liquid and the constant K is a measure of the volatility of the vapour from solution. This equation shows that absorption can never be complete, and, as V increases, the exponential term in the equation tends to disappear; the efficiency is then inversely proportional to the volume of air sampled. At this point the concentration of vapour in solution is in equilibrium with the concentration in the gas phase and is a limiting value that cannot be increased by bubbling a further volume of air through the liquid. The ratio between these two concentrations is a measure of the constant K; it is apparent that the greater the value of K the lower the efficiency, which may be improved by cooling the solvent if this achieves a decrease in K. The efficiency may also be increased by increasing v, the volume of the absorbing liquid. The equation does not include terms for the concentration of vapour in the atmosphere or for the rate of sampling, for it is assumed that the concentration of vapour within each air bubble reaches equilibrium with the concentration in solution during its passage through the liquid. The efficiency given by this equation is, therefore, the maximal theoretical figure; the efficiency achieved in practice may be less than this and may to some extent be affected by the design of the absorber and the rate of sampling.

Ethylene oxide atmospheres have been used in an experimental investigation into the effect of the sampling conditions on efficiency. Ethylene oxide is suitable for this purpose, as, although completely miscible with water, its volatility from aqueous solution is appreciable. In one method it was necessary to use two absorbers in series cooled in ice - water to obtain an adequate efficiency of absorption.[4]

ABSORPTION OF GASES AND VAPOURS BY CHEMICAL REACTION—

When a gas or vapour is absorbed from air by chemical reaction with a liquid, complete retention may be achieved however large the volume of the air sample, provided that the reaction is sufficiently rapid in relation to the rate of sampling and that a sufficient excess of the reagent remains in the liquid. A slow reaction may result in an extremely low efficiency of absorption, which cannot be improved by decreasing the volume of the air sample. The former type of reaction is unsuitable for a study of the effect of sampling conditions; the latter requires prolonged contact between air and liquid for complete absorption and should not be used with bubbler-type absorbers.

The efficiency of absorption of a gas or vapour by chemical reaction depends on the probability of successful collisions with molecules of reagent at the air - liquid interfaces. For a given concentration of reagent this will depend on the average volume of the air bubbles, on the length of the column of liquid through which the bubbles must pass and the rate at which they rise through the liquid. All of these will be affected by the design of the bubbler; in particular, the effect of bubble size will be important, as this influences both the total area of bubble surface and the rate at which the bubbles rise. The efficiency will be a function of the rate of air sampling only if this produces a change in bubble size; an increase in the rate

brought about by an increase in the number of bubbles passing in unit time without an increase in the average size of bubble is not likely to be attended by a decrease in efficiency.

A number of reactions have been studied for their suitability in the investigation of the effect of sampling conditions. Some of the systems tested, such as the absorption of chlorine in *o*-tolidine solution, are so rapid that high efficiency is attained even at rapid sampling rates and is maintained even at low concentrations of *o*-tolidine; the efficiency decreases only when the amount of reagent in solution approaches that of the chlorine in the air sample. Other reactions, such as the absorption of aniline vapour in dilute hydrochloric acid, are complicated by retention of aniline being due partly to reaction with acid and partly to solution, as an appreciable amount is retained in the absence of acid. An unexpected complication was observed in the absorption of benzene vapour in nitric - sulphuric acid mixtures; at low concentrations of nitric acid there was evidence of the reaction taking place in two stages. The reaction finally chosen was the absorption of chlorobenzene vapour in a dilute solution of paraformaldehyde in sulphuric acid; the chemical nature of this reaction is obscure and is presumably the same as that occurring in the reaction of aromatic hydrocarbons with formaldehyde - sulphuric acid ("formolite") mixture[4]; this modification of the older procedure has been found to have considerable advantages and is being developed as a general method for the determination in air of aromatic hydrocarbons and certain of their derivatives.

RETENTION OF PARTICULATE MATTER—

There is no doubt that the design of the absorber plays a most important part in the retention of particulate matter by a liquid. The problems associated with the determination of dust, mists and fumes in the atmosphere have been discussed in detail[5] and will be only briefly referred to here. A liquid absorber is highly efficient for retaining particles only when the velocity of the air at the jet approaches that of sound and the particles impinge with high velocity on a surface in the liquid; the sudden change in kinetic energy results in the virtually complete trapping of all particles having a diameter greater than 1 μ. Such an absorber is known as an impinger, and the best known design is the midget impinger, adopted by the United States Bureau of Mines.[6]

EXPERIMENTAL

PREPARATION OF TEST ATMOSPHERES—

Test atmospheres containing ethylene oxide and chlorobenzene were prepared dynamically by the procedure established in these laboratories. Solutions were atomised at a known rate into a metered stream of air by means of a controlled fluid-feed atomiser[7] operated by a slow-motion injection apparatus that had been modified by the makers (C. F. Palmer Ltd.) to provide a vertical drive. For the ethylene oxide atmosphere, the air supply to the atomiser was humidified by bubbling through water; for chlorobenzene it was dried by passage through a tower containing silica gel. The atomiser assembly differed slightly from that previously described by having the atomiser head either fused directly to the syringe or attached to it by means of a standard-taper joint. The solution of ethylene oxide was prepared in water, and that of chlorobenzene in ethanol. The air from the atomiser entered a mixing chamber from which the bulk ran to waste, and a T-connection controlled by a stopcock was provided for collecting the air sample.

Air samples at rates below 0·5 litre per minute were withdrawn by means of a water aspirator; for rates of 0·5 litre per minute or above a vacuum pump was used, controlled by means of a suitable orifice plate and calibrated pressure gauge.

MEASUREMENT OF BUBBLING RATE—

To determine the relationship between the flow of gas through a liquid absorber and the rate of disengagement of bubbles, an absorber was connected by a short length of rubber tubing to a T-piece, one arm of which was connected to an oxygen cylinder through a flow-meter and the other to a capacitance manometer. The gas was allowed to pass through the liquid at the required rate, and the pressure changes produced during the disengagement of bubbles were transduced by means of the manometer, a circuit designed by Alexander[8] being used, and displayed on one beam of a double-beam cathode-ray oscilloscope. The output of a sine-wave oscillator with a frequency of 15 cycles per second was displayed on the other beam, and both traces were recorded photographically. By this means the bubbling rate was calculated and hence, from the measured gas flow, the average bubble diameter was determined.

DESIGN OF ABSORBERS—

The three types of absorber used in this investigation are shown in Fig. 1.

Type A—This was an all-glass absorber having a flat base; it could serve as a bubbler or as an impinger. The external dimensions of the outer tube were 2·7 cm × 18·0 cm; the air-inlet tube terminated in a jet having an internal diameter of 1 mm, situated 0·5 cm from the flat base.

Type B—This was similar to type A, but the external diameter of the tube was restricted to 1·45 cm.

Type C—The external dimensions of this absorber were similar to those of type A, but the jet was replaced by an annular sintered-glass air distributor (porosity No. 1).

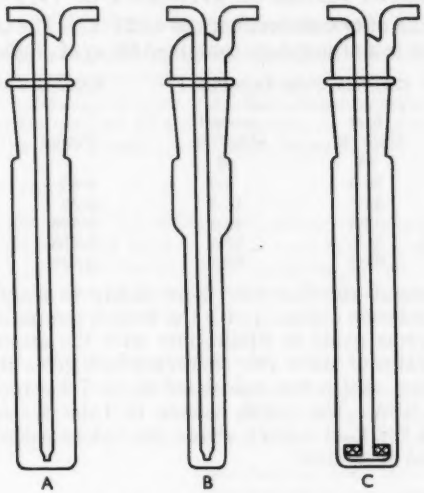

Fig. 1. Design of absorbers

ANALYTICAL METHODS—

Ethylene oxide—Two absorbers of the type being investigated, each containing 10 ml of water, were immersed in a water bath at 25° C and attached in series to the sampling point of the test-atmosphere generator. After the air sample had been drawn through the absorbers, they were detached and 1 ml of 0·1 *M* periodic acid was added to the contents of each. The solutions were heated for 40 minutes on a bath of boiling water, and the analysis was then completed as described previously.[9] The concentration of ethylene oxide was determined from the measured optical density by reference to a standard graph plotted from the results obtained when ethylene oxide solutions having known concentrations were submitted to the same procedure. For measuring the higher ethylene oxide concentrations the solution in the absorber was suitably diluted and correspondingly larger amounts of reagents were used.

Chlorobenzene—The atmosphere was sampled through two absorbers in series, each containing 15 ml of a solution of 10 mg of paraformaldehyde in 100 ml of concentrated sulphuric acid. The optical density at 485 mμ was measured 5 minutes after the end of the sampling period, cylindrical cells 2·5 cm in diameter being used. Each point for the standard graph was determined as follows. An absorber (type C) containing 15 ml of paraformaldehyde - sulphuric acid solution was attached to a short length of glass tubing containing a glass-wool plug, and, with a current of air passing through the absorber at 0·2 litre per minute, a measured volume of an ethanolic solution of chlorobenzene was placed on the plug by means of a micrometer syringe. After 2 litres of air had passed, the optical density was measured as described above.

Results for ethylene oxide

The concentration used in all these experiments was 50 μg of ethylene oxide per litre of air. The efficiency of an absorber under the experimental conditions was taken as the ratio between the amount of ethylene oxide found in the first absorber and the total amount present in the air sample.

Effect of sample volume—

Volumes of the test atmosphere were drawn through two absorbers (type A) in series at 0·5 litre per minute; the amounts of ethylene oxide found in each absorber are shown in Table I. As the sample volume increased, the amount in the first absorber rose to a constant

Table I

Effect of sample volume on efficiency of type A absorbers

Each result is the mean of two determinations at 25° C. The sampling rate was 0·5 litre per minute and the test atmosphere contained 50 μg of ethylene oxide per litre

Volume of sample, litres	Ethylene oxide found in— first absorber, μg	Ethylene oxide found in— second absorber, μg	Efficiency of first absorber: Found	Efficiency of first absorber: Theoretical (K = 7·9)
0·5	20·5	5·0	0·82	0·845
1·0	34·5	16·5	0·69	0·69
2·0	52·5	30·0	0·525	0·502
5·0	64·5	58·5	0·258	0·245
10·0	63·0	63·0	0·126	0·126

value and that in the second absorber rose more slowly to reach the same figure. This limiting value in 10 ml of solution obtained with the 10-litre sample may be taken to represent the concentration of ethylene oxide in equilibrium with the atmospheric concentration of 50 μg per litre, and the ratio of these two concentrations gives the value of the constant K in the efficiency equation, which was calculated to be 7·9, expressed as micrograms per millilitre/micrograms per litre. The fourth column in Table I shows the efficiency figures found experimentally and the final column shows the values calculated from the efficiency equation; these are in good agreement.

Effect of sampling rate—

Some 2-litre samples of the test atmosphere were drawn through two absorbers (type A) at different sampling rates; the ethylene oxide contents of the absorbers and the efficiency of the first absorber are shown in Table II. These results show that there is no change in efficiency up to 2 litres per minute, but that there is a slight decrease at 4 litres per minute.

Table II

Effect of sampling rate on efficiency of type A absorbers

Each result is the mean of two determinations at 25° C. The volume of sample used was 2 litres and the test atmosphere contained 50 μg of ethylene oxide per litre

Sampling rate, litres per minute	Ethylene oxide found in— first absorber, μg	Ethylene oxide found in— second absorber, μg	Efficiency of first absorber
0·5	48	30	
1·0	48	25	0·48
2·0	48	27	
4·0	42	24	0·42

Effect of absorber design—

A 2-litre sample of the test atmosphere was drawn at 0·5 litre per minute through different types of absorber, connected in pairs in series; the results are shown in Table III. The efficiency obtainable with a type A absorber was not improved by filling it with glass beads approximately 2 mm in diameter nor is that of a type C absorber any greater.

Table III

Effect of absorber design on efficiency

Each result is the mean of two determinations at 25° C. The sampling rate was 0·5 litre per minute, the volume of sample used was 2 litres and the test atmosphere contained 50 μg of ethylene oxide per litre

Absorber	Ethylene oxide found in— first absorber, μg	second absorber, μg	Efficiency of first absorber
Type A	48	30	0·48
Type A filled with glass beads ..			
Type C	48	37	0·48

Results for chlorobenzene

Atmospheres containing about 350 μg of chlorobenzene per litre were used in all experiments save those involving a sampling rate of 5 litres per minute; in these tests, the concentration was approximately 70 μg per litre. As the concentrations showed some variation, the figure taken for the total content of the air sample in the efficiency calculation was the sum of the contents of the two absorbers in each experiment.

Effect of absorber design—

The efficiencies obtained with the different types of absorber are shown in Table IV. The best results were obtained with type C, which contains a sintered-glass air distributor. The efficiency of a type A absorber can be appreciably improved by decreasing its diameter (type B), but little advantage was obtained by filling it with glass beads.

Table IV

Effect of absorber design on efficiency for chlorobenzene atmosphere

Each result is the mean of two determinations with two absorbers in series. The sampling rate was 0·2 litre per minute, the volume of sample used was 1 litre and the test atmosphere contained approximately 350 μg of chlorobenzene per litre

Absorber	Chlorobenzene found in— first absorber, μg	second absorber, μg	Efficiency of first absorber
Type A	250	58	0·81
Type A filled with glass beads ..	285	48	0·86
Type B	330	24	0·93
Type C	352	15	0·96

Effect of sampling rate—

The results in Table V show that the efficiency of a type A absorber diminishes as the sampling rate increases. This decrease may be correlated with the increase in bubble size occurring when the sampling rate is increased, as shown by the results below for a type A absorber containing 15 ml of sulphuric acid—

Sampling rate, litre per minute ..	0·029	0·058	0·10	0·205	0·38
Bubble diameter, mm	4·6	5·2	5·8	6·2	7·2

Above a sampling rate of 0·4 litre per minute regular bubble formation can no longer be detected on the tracing from the cathode-ray oscilloscope.

Discussion of results

The main conclusion to be drawn from this investigation is that, although the design of a liquid absorber is of prime importance in the sampling of particulate matter in the atmosphere, it is not usually of great importance in the determination of gases and vapours. This applies in particular to the absorption of gases and vapours by solution, when the main factors controlling the efficiency of absorption are the volatility of the substance from solution and

the volume of the air sample. The theoretical equation relating the efficiency of absorption to the experimental variables has been confirmed by experiments with ethylene oxide, and, in order to maintain the efficiency of a single absorber at more than 80 per cent., it is necessary for the term v/VK, in which v is the volume of liquid in the absorber, V is the volume of the air sample and K is the volatility constant, to be less than 2·2. In order to achieve this it is necessary to use either a small sample of air, which requires a sensitive analytical method, or a large volume of liquid in the absorber, which may necessitate an extraction before the final measurement. Alternatively, the value of K can be decreased by cooling the liquid, or two liquid absorbers in series may be used. In one method for determining ethylene oxide,[4] which requires a large sample of air, as it is based on a relatively insensitive titrimetric procedure, it was necessary to recommend two absorbers in series cooled in ice - water; in the method used in this investigation, which involves a much more sensitive colorimetric procedure[9] and therefore requires a much smaller sample of air, the efficiency was adequate with one absorber at room temperature.

TABLE V

EFFECT OF SAMPLING RATE ON EFFICIENCY OF TYPE A ABSORBER FOR CHLOROBENZENE ATMOSPHERE

Each result is the mean of two determinations. The volume of sample used was 1 litre and the test atmosphere contained approximately 350 μg of chlorobenzene per litre

Sampling rate, litres per minute	Chlorobenzene found in— first absorber, μg	second absorber, μg	Efficiency of first absorber
0·05	315	22	0·93
0·1	285	34	0·89
0·2	250	58	0·81
0·5	246	86	0·74
1·0	205	81	0·72

The effect of sampling rate is not apparent in absorption by solution until the rate is such that the concentration in the air as it passes through the solution fails to reach equilibrium with the concentration in solution. With ethylene oxide, this was noticeable at a sampling rate of 4 litres per minute and may be connected with the failure of the regular disengagement of bubbles at the jet at these higher rates. An improvement could be achieved here by a change in the design of the absorber, possibly a narrower tube with a longer liquid path for the bubbles might gain some advantage, but more is to be expected from an air distributor to break up the air flow to finer bubbles. A sintered-glass disc may be satisfactory, but a lower pressure drop, which may be important at high sampling rates, would be attained by replacing the jet of the air-inlet tube by a bulb pierced with a ring of holes about 1 mm in diameter. The effect of sampling rate is more apparent in a few of the methods involving absorption by chemical reaction, when the rate of the reaction is not so fast that complete efficiency is attained whatever the sampling conditions. An example of such a reaction is the absorption of chlorobenzene in paraformaldehyde - sulphuric acid, in which the efficiency decreases as the sampling rate increases; this can be correlated with the attendant increase in bubble size, giving a smaller surface per unit volume and a more rapid rise through the liquid, although there is insufficient evidence to derive a quantitative relationship. The efficiency of the limited number of methods in this category can be increased by using an absorber having a longer column of effective liquid or by breaking up the air stream into small bubbles by means of a sintered-glass distributor.

A number of reported methods involve an absorber filled with glass beads. This might be expected to increase the efficiency of solution absorption by preventing mixing and so producing a concentration gradient in the solution and of reaction absorption by retarding the passage of bubbles through the liquid. No advantage has been found experimentally, probably owing to channelling of the bubbles through the glass beads.

Technical assistance in this investigation was provided by Mr. Z. S. Bérczy and Mr. T. V. H. Chalker.

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Received *July 31st*, 1959

Quantitative Paper Chromatography of Inorganic Ions in Soils and Plants

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Copper, cobalt, nickel and zinc are separated by paper chromatography. The first three are determined directly by means of an automatic-recording reflectance densitometer. The method is applied to certain soils and plant materials.

Separation by paper chromatography of inorganic ions in plants and soils before their quantitative determination is a technique recently used by some investigators[1,2,3]; it has also been used in geochemical prospecting.[4] After separating the ions one from another, they have been determined one at a time colorimetrically[1,2,3] or the extent of the bands or spots has been compared visually after spraying with suitable mixed reagents.[3] We have attempted to combine the virtues of the standard methods[1,2,3,5,6]—concentration techniques for soil and plant micronutrient analysis and paper chromatography—with automatic densitometry.

A brief report has been given elsewhere.[7]

Method

Reagents—

All the reagents used were of analytical-reagent grade, unless otherwise stated. The water used throughout was distilled in a borosilicate-glass still, *i.e.*, of arc-spectrography standard.

Stock solutions—These were prepared by dissolving a suitable pure salt of nickel, cobalt, copper, zinc or molybdenum in distilled water (1 mg per ml for each element).

Standard solutions—The standard series were—

(*i*) Cobalt: 0·05, 0·10, 0·20, 0·30 and 0·40 μg per 10 μl.
(*ii*) Nickel, cobalt, copper and zinc mixture: 0·40, 0·80, 1·60 and 3·20 μg per 10 μl.
(*iii*) Nickel, cobalt, copper and zinc mixture: 1, 2, 3, 4 and 8 μg per 10 μl.

All paper was dried at 40° C for 30 minutes.

Chromatography solvent—Acetone - ethyl acetate - 6 *N* hydrochloric acid mixture (9:9:2) (for zinc, copper, cobalt and nickel separation), prepared from purified reagents.

Rubeanic acid solution—A 0·1 per cent. ethanolic solution of rubeanic aid (for nickel, copper and cobalt).

1-*Nitroso*-2-*naphthol solution*[8]—An aqueous alkaline solution containing 0·5 mg per ml (for cobalt).

Chloroform—Laboratory-reagent grade chloroform distilled over dithizone before use.

Dithizone solution—A solution of dithizone in chloroform, containing 25 mg per 100 ml.
Dimethylgloxime solution, 5 per cent., aqueous.
Tamm's buffer solution—Ammonium oxalate (24·90 g) and 12·60 g of oxalic acid dissolved in 1 litre of distilled water to give a solution of pH 3·3.
Ammonium citrate solution, 20 per cent.—Purified by extraction with a solution of dithizone in chloroform.
Hydrochloric acid, 6 N, 10 per cent., 3 N and 0·1 N.
Sulphuric acid—Concentrated acid for food analysis (low lead content).
Perchloric acid, sp.gr. 1·54.
Nitric acid—Concentrated ordinary grade distilled from a Pyrex-glass still before use.
Ammonium hydroxide—Ammonia gas from a cylinder, dissolved in distilled water to give a saturated solution.
Potassium iodide solution, 50 per cent., aqueous.
Tartaric acid solution, 50 per cent., aqueous.
Sodium thiosulphate solution, 10 per cent., aqueous.

APPARATUS—

Chromatography tubes—Giant test-tubes, 20 inches high × 3 inches diameter, held vertically in a rack with a capacity for eight tubes, were closed at the top by rubber stoppers carefully wrapped in polythene sheets. These stoppers carried glass hooks from which to suspend the paper strips.
Densitometer—A double-beam automatic-recording and integrating reflectance densitometer was used (obtained from Joyce, Loebl & Co., Newcastle-upon-Tyne, 1958 model).

PAPER CHROMATOGRAPHY—

An appropriate volume (10 μl) was applied in one application by micropipette as a spot of diameter about $\frac{1}{4}$ inch about $1\frac{1}{2}$ inches from one end of the paper strip (Whatman No. 54). The solvent system (20 ml) was placed in the tube and the paper strip was allowed to dip $\frac{1}{4}$ inch into the liquid after the spot had dried in air. The strip was developed by an ascending-solvent technique.[9] After development for 6 hours the strip was air-dried, exposed for 15 minutes to ammonia fumes in a second tube to neutralise the acid and then sprayed with the appropriate detection reagent (0·1 per cent. solution of rubeanic acid for copper, cobalt and nickel; 0·05 per cent. solution of 1-nitroso-2-naphthol for low levels of cobalt).

CALIBRATION CURVES—

Three sets of curves were prepared by the application of small volumes (~ 10 μl) to chromatography paper by micropipette.

(*i*) Low concentrations of cobalt in the range 0·05 to 0·4 μg per μl (detection reagent, 0·05 per cent. solution of 1-nitroso-2-naphthol).
(*ii*) Medium concentrations of nickel, cobalt and copper in the range 0·4 to 3·2 μg per 10 μl.
(*iii*) High concentrations of nickel, cobalt and copper in the range 1 to 8 μg per 10 μl (0·1 per cent. ethanolic solution of rubeanic acid was used as the detection reagent for (*ii*) and (*iii*)).

INTERPRETATION OF CHROMATOGRAM—

(*a*) *Densitometry*—The method was similar to that used for spot-test analysis,[10] except that concentration was related to the area under the curve ("integrator steps"). The distance from the base line to the integrated steps was maintained at 4·5 cm.

(*b*) *Evaluation of the recording*—The perpendiculars from the intersection of the tangents from the curves with the base line showed the number of "integrator steps" corresponding to the area under the curve. The area under the curve was plotted against concentration (μg per 10 μl).

ZINC—

The coloured band on the paper chromatogram corresponding to zinc was cut off, dry ashed at 450° C, and determined colorimetrically[1] at 578 mμ in a 2-cm cell with a Unicam SP600 spectrophotometer.

PROCEDURE FOR SOILS—

Extraction of 10 *g of soil with* 0·5 N *acetic acid*—A 10-g portion of air-dried soil (2 mm) was shaken with 400 ml of 0·5 *N* acetic acid for 1½ hours, and the solution was filtered through acid-washed Whatman No. 54 filter-paper into a 1-litre Pyrex-glass beaker. The solution was first evaporated to a small volume on a hot-plate, and then to dryness on a water bath. Two or three 5-ml portions of nitric acid were added to oxidise organic matter (evaporating to dryness after each addition), and the residue was dissolved in 40 ml of 3 *N* hydrochloric acid, with heating on a steam-bath for 15 minutes. The solution was then filtered through a 9-cm Whatman No. 41 filter-paper into a 250-ml Pyrex-glass beaker, the filter-paper being washed with hot water. A 20-ml portion of purified 20 per cent. ammonium citrate solution was added to the filtrate, and the pH was adjusted to 8·3. This solution was exhaustively extracted with dithizone in chloroform, with vigorous shaking in a machine for 5 minutes, at least seven times, complete extraction being indicated by an unchanged green colour at the final dithizone addition. The residual dithizone was extracted after neutralisation with fresh chloroform, and this extract was added to the previous ones. The pH of the residual solution was then adjusted to 8·0, and 2 ml of 5 per cent. aqueous dimethylglyoxime solution were added. The nickel complex was extracted with, usually, three 5-ml portions of chloroform until no nickel remained. All the chloroform extracts were then combined, the chloroform was removed by distillation, the residue dissolved repeatedly in 6 *N* hydrochloric acid, evaporating after each addition, and the solution finally evaporated to dryness. The residue in a 150-ml evaporating flask was dissolved in 0·3 ml of 6 *N* hydrochloric acid, and then washed with further small amounts of the acid (0·2 ml). The solution and washings were collected in a 3-ml bottle, the volume was reduced to 0·15 ml by evaporation on a hot-plate at 70° C, the bottle was set aside to cool in a desiccator for 15 minutes, and then weighed. The amount ($\sim 10\ \mu l$) withdrawn for chromatography was found by weight difference.

Extraction of 50 *g of soil with* 0·5 N *acetic acid*—A 50-g portion of air-dried soil (2 mm) was extracted with 800 ml of 0·5 *N* acetic acid in the same way as the 10-g sample. A 20-ml portion of purified 20 per cent. ammonium citrate solution was used as before. Paper chromatography showed the presence of cobalt in these extracts.

Extraction with 0·1 N *hydrochloric acid*—A 10-g portion of air-dried soil (2 mm) was extracted with 100 ml of 0·1 *N* hydrochloric acid for 1½ hours, and the solution was filtered through Whatman No. 54 filter-paper. The first 10 ml of filtrate were rejected, but the bulk of the filtrate (80 ml) was collected. A 20-ml portion of purified 20 per cent. ammonium citrate solution was added, and the filtrate was treated as described for extraction with acetic acid.

PROCEDURE FOR PLANTS—

A 5-g portion of plant material was digested in a Kjeldahl flask with a mixture of 10 ml of concentrated nitric acid, 4 ml of concentrated sulphuric acid and 1 ml of concentrated perchloric acid. When the solution was cool, some distilled water was added, the solution was heated and kept hot for 30 minutes. The solution was then filtered through acid-resistant Whatman No. 541 filter-paper into a 100-ml calibrated flask and diluted to the mark with distilled water. A 40-ml portion of this solution was used for dithizone and dimethylgloxime extractions after the addition of purified 20 per cent. ammonium citrate solution. The solution for chromatography was then prepared as described for the acetic acid extract of soils.

Subsidiary procedure for cobalt[3]—A 20-g portion of plant material was ashed overnight in a silica basin at 450° C. The ash was then moistened with a few millilitres of distilled water and 10 ml of 3 *N* hydrochloric acid, and the solution evaporated to dryness and heated on a hot-plate for 30 minutes at 90° C. This operation was repeated three times to ensure complete dehydration of the silica. The residue was dissolved in 10 ml of 3 *N* hydrochloric acid, the solution was filtered through a Whatman No. 54 filter-paper, which was then washed with small portions of 3 *N* hydrochloric acid, the filtrate was evaporated to dryness on a water bath, and the residue was treated with 0·5 to 1 ml of 6 *N* hydrochloric acid. The basin, covered with a watch glass, was set aside for 3 hours with occasional stirring. A small portion (10 μl) of this extract was taken for chromatography, a 0·05 per cent. solution of 1-nitroso-2-naphthol being used as detection reagent.

Paper chromatography showed the presence of cobalt in these extracts.

Results

A chromatogram and its densitometer tracing are shown in Fig. 1. The standard curves of the various concentration ranges are shown in Figs. 2, 3 and 4.

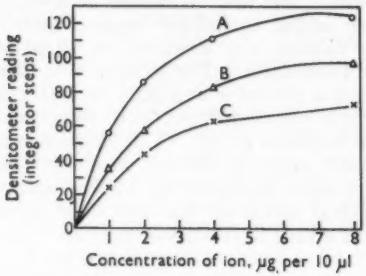

Fig. 2. Standard graphs for medium to high concentrations of: curve A, nickel; curve B, copper; curve C, cobalt

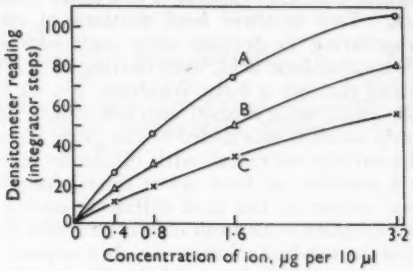

Fig. 3. Standard graphs for medium to low concentrations of: curve A, nickel; curve B, copper; curve C, cobalt

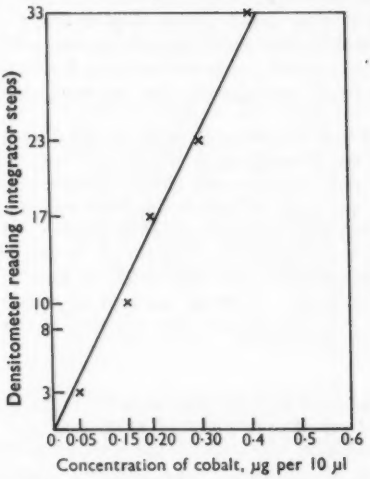

Fig. 4. Standard graph for very low concentrations of cobalt

Samples of soils on Silurian shale from Coed Coch, Denbighshire, were analysed for nickel, copper and cobalt. The results of these analyses are shown in Tables I and II.

Table I

Nickel, copper and cobalt found in 0·5 *N* acetic acid extract of Coed Coch soil

A 10-g portion of soil was used

Sample No.	Locality (field)	Nickel found, p.p.m.	Copper found, p.p.m.	Cobalt found, p.p.m.
8	Cae Tarw (short grass)	0·68	0·47	<0·1
9	Cae Tarw (long grass)	0·80	0·30	<0·1
10	Ffridd (long grass)	0·40	—	<0·1
11	Ffridd (short grass)	0·40	0·24	<0·1

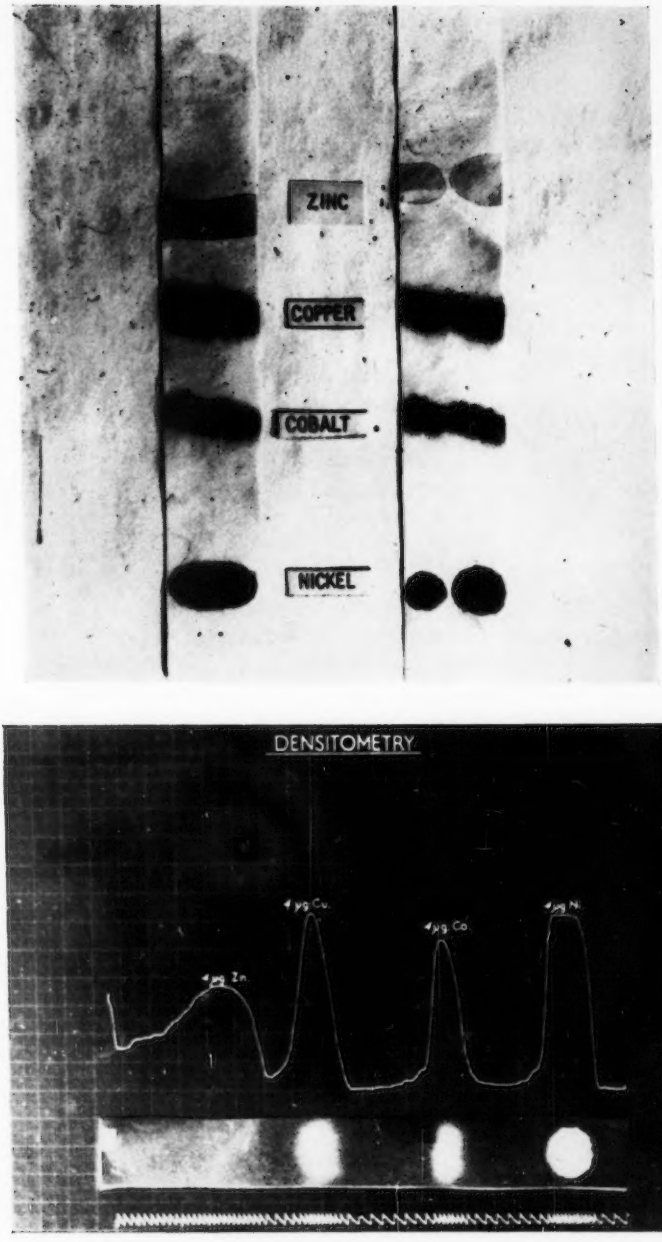

Fig. 1. One-dimensional chromatograms of nickel, copper, cobalt and zinc and a corresponding densitometer tracing. Chromatograms run on Whatman No. 54 filter-paper with acetone - ethyl acetate - 6 *N* hydrochloric acid (9:9:2) as solvent

[To face p. 206

TABLE II

NICKEL, COPPER AND COBALT FOUND IN 0·1 *N* HYDROCHLORIC ACID EXTRACT OF COED COCH SOIL

A 10-g portion of soil was used

Sample No.	Locality (field)	Nickel found, p.p.m.	Copper found, p.p.m.	Cobalt found, p.p.m.
8	Cae Tarw (short grass)	0·95	0·33	<0·1
11	Ffridd (short grass)	0·86	0·32	<0·1

Cobalt was added to a soil and a 0·5 *N* acetic acid extract; the recoveries were—

	Soil	Solution
Cobalt added, μg	2	1
Cobalt recovered, μg	1·9	0·8

Plant material from the various sites was analysed and the results are shown in Table III.

TABLE III

NICKEL, COPPER AND COBALT FOUND IN PLANT MATERIAL FROM VARIOUS SITES

A 5-g portion of plant material was used

Sample No.	Locality (field)	Nickel found, p.p.m.	Copper found, p.p.m.	Cobalt found, p.p.m.
8	Cae Tarw (short grass)	6·0	18·0	<0·1
9	Cae Tarw (long grass)	2·3	9·9	<0·1
10	Ffridd (long grass)	3·3	13·9	<0·1
11	Ffridd (short grass)	3·0	11·4	<0·1

DISCUSSION OF THE METHOD

The method requires less than 1 g of soil for nickel, copper and zinc (just over 3 g for low levels of cobalt) and only about one-third of a gram of plant material (just over 1 g for low levels of cobalt). It is thus more sensitive and less time-consuming than is arc spectrography. Though we have dealt only with nickel, copper and cobalt, there seems to be no real obstacle to an extension to other ions for simultaneous determination.

Preliminary investigations show that many of the micronutrients in the concentrates used for arc spectrography are separable by paper chromatography on a single strip.

Zinc was present in amounts rather inconvenient for compact chromatographic separation and subsequent densitometry. Addition of smaller amounts of extract would probably allow densitometry. However, good results were obtained when the zinc band was cut out, ashed and determined colorimetrically. Molybdenum, although giving a compact spot on the paper chromatogram did not give quantitative colour yields with the mixed alizarin - rubeanic acid - salicyl aldoxime reagent on paper under the conditions employed. The medium and high levels of copper, nickel and cobalt give reasonably linear relationships if the concentration is plotted on a $\log_2$ scale.

One of us (C.B.C.) is grateful to the University of Wales for the tenure of an I.C.I. Research Fellowship.

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Received *July 6th*, 1959

Separation of Niobium and Tantalum together from Titanium

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The preferential formation of a stable complex of titanium with a mixture of oxalate and ethylenediaminetetra-acetic acid in alkaline medium is utilised to separate niobium and tantalum together from titanium under suitable conditions.

Titanium interferes seriously in all available precipitation methods for the individual separation of niobium and tantalum. It is therefore useful to remove this element from the earth acids before separating them individually, and Atkinson, Steigman and Hiskey[1] have shown the complexity of this problem. The earth acids can be separated from titanium by a few chemical procedures,[2 to 8] but separation is not sharp.

Niobium, tantalum and titanium can be separated together from minerals by precipitation with tannic acid from oxalate solutions, other cations being masked by using the disodium salt of ethylenediaminetetra-acetic acid (EDTA).[9] The separation of these three elements from other metals in hard alloys can be effected by precipitation with ammonium hydroxide in presence of glycerine, EDTA again being used to mask other metals.[10] The quantitative precipitation of these elements as hydrated oxides from oxalate solutions has been reported,[11] and Přibil and Schneider[12] have described the quantitative precipitation of titanium with ammonium hydroxide in presence of EDTA. On the basis of these facts, attempts were made in this laboratory to use ammonium hydroxide as precipitant instead of tannic acid[9]; the experiments showed that most of the titanium was not precipitated. This indicated the formation of a fairly stable complex of titanium in alkaline medium when both oxalate and EDTA were present, and this paper describes the application of this observation to separate the earth acids from titanium.

Experimental

Reagents—

Solution of earth acids—A stock solution of niobium and tantalum was prepared from a sample of niobite - tantalite previously found to contain 81·6 per cent. of total earth acids (Nb_2O_5 *plus* Ta_2O_5) and traces of titania. The sample was fused with potassium hydrogen sulphate and hydrolysed with tartaric acid twice. The final hydrolysis product was ignited, fused with potassium hydrogen sulphate and then dissolved in a mixture of oxalic and hydrochloric acids, a concentration of 4 per cent. w/v of oxalic acid being maintained. A 25-ml portion of this solution, when treated with tannic acid, gave 83·5 mg of mixed-oxide precipitate, which was analysed for titania. The usual peroxide method did not indicate the presence of titanium, and this method was used in all subsequent determinations of titania in R_2O_5.

Titanium solution—Titania was fused with potassium hydrogen sulphate, and a solution containing 50 mg of titania per 20 ml was prepared by dissolving the melt in 5 per cent. v/v sulphuric acid.

Ammonium hydroxide—This reagent was freshly prepared by absorbing ammonia in distilled water until the specific gravity of the solution was 0·90. This solution was diluted to twice its volume.

EDTA solution—A 10 per cent. w/v aqueous solution of disodium ethylenediaminetetra-acetate dihydrate.

All other reagents used were of either Merck C.R. or AnalaR grade.

Preliminary experiments—

Preliminary experiments on the precipitation of the mixture of earth acids by ammonium hydroxide, oxalate concentration and pH being varied, showed that the optimum pH for quantitative precipitation increased with increase of oxalate concentration; precipitation

was quantitative at pH 8·0 in 4 per cent. w/v oxalic acid solution. In all subsequent precipitations, the concentration of oxalic acid was maintained at or below 4 per cent. w/v and the addition of ammonium hydroxide was continued until a pink colour was obtained with phenolphthalein (freshly added in each test).

EFFECT OF EDTA AND OXALIC ACID—

The effect of the relative proportions of EDTA and oxalic acid on the quantitative precipitation of the earth acids was studied; the results are shown in Table I. When the amount of EDTA present was greater than that of oxalic acid, precipitation was always incomplete. When the ratio of EDTA to oxalic acid was between 1 to 1 and 1 to 2, the amount of precipitate formed was not reproducible, although precipitation was quantitative when the solution was set aside overnight before filtration. (This was not desirable, as it was time-consuming and might have increased co-precipitation of titanium.) When the ratio was maintained at or above 1 to 3, precipitation was consistently quantitative and it was unnecessary to set the solution aside overnight.

TABLE I

EFFECT OF RATIO OF EDTA TO OXALIC ACID ON PRECIPITATION OF EARTH ACIDS

Each solution contained 83·5 mg of earth acids, as R_2O_5, in a volume of about 400 ml; in experiment No. 7 the volume of solution was about 500 ml. The filtrates in experiments Nos. 1 to 5, when tested with tannic acid, were found to contain earth acids

Experiment No.	Amount of EDTA present, g	Amount of oxalic acid present, g	Amount of R_2O_5 precipitated, mg	Error, mg
1	2·0	1·0	79·0	−4·5
2	4·0	2·0	80·5	−3·0
3	1·0	1·0	82·0	−1·5
4	1·0	1·0	82·7	−0·8
5	7·5	15·0	82·7	−0·8
6	2·0	5·0	83·1	−0·4
7	2·0	6·0	83·8	+0·3
8	5·0	19·0	84·0	+0·5
9	1·0	5·0	83·5	0·0
10	2·0	10·0	83·7	+0·2

The EDTA concentration was kept constant and the ratio of EDTA to oxalic acid was varied to study the effect on the separation of earth acids from titanium. The results (see Table II) showed that the optimum ratio was 1 to 3 and that an increase in oxalate concentration resulted in greater co-precipitation of titanium. In all subsequent experiments this optimum ratio was maintained.

TABLE II

EFFECT OF RATIO OF EDTA TO OXALIC ACID ON SEPARATION OF EARTH ACIDS FROM TITANIUM

Each solution contained 83·5 mg of earth acids, as R_2O_5, 50 mg of TiO_2 and 2·5 g of EDTA

Amount of oxalic acid present, g	Ratio of oxalic acid to EDTA	Amount of R_2O_5 precipitated, mg	Amount of TiO_2 in R_2O_5 precipitate, mg
6·0	2·4	90·3	6·7
7·5	3·0	86·5	2·7
8·5	3·4	86·2	2·7
10·0	4·0	88·9	5·2
11·0	4·4	91·8	8·4

The amount of complexing mixture used to precipitate a fixed amount of earth acids and titanium was then varied. The results showed that the amount of titanium accompanying the earth acids decreased as the amount of complexing mixture used increased. However, if more than 5 and 15 g of EDTA and oxalic acid, respectively, in a total volume of about 400 ml were used, salts crystallised during filtration. Further, the decrease in the amount of titania accompanying the earth acids was practically negligible when the amounts of EDTA and

oxalic acid were increased above 4 and 12 g, respectively. A re-precipitation was tried under the same conditions, but about 1 mg of titania was still carried down by the precipitate of earth acids. The results of these experiments are shown in Table III.

Table III

Effect of variation in amount of complexing mixture used

Each solution contained 83·5 mg of earth acids, as R_2O_5, and 50 mg of TiO_2

Amount of EDTA present, g	Amount of oxalic acid present, g	Amount of R_2O_5 precipitated, mg	Amount of TiO_2 in R_2O_5 precipitate, mg
Single precipitation—			
1·0	3·0	93·5	10·2
2·0	6·0	89·9	6·2
3·0	9·0	88·5	5·1
4·0	12·0	86·5	3·0
6·5	21·0	85·9	2·6
Two precipitations—			
2·0	6·0	84·5	1·1
5·0	15·0	84·3	0·9
		84·1	0·7
		83·9	0·4

Method

Procedure—

Fuse the mixed oxides of niobium, tantalum and titanium with about 5 g of potassium hydrogen sulphate, allow the melt to cool, and extract with 150 ml of hot 10 per cent. w/v solution of oxalic acid. Add 5·0 g of EDTA, as a solution, and 50 ml of ammonium chloride solution (saturated at laboratory temperature), dilute to about 350 ml, and boil. Add ammonium hydroxide carefully, with continuous stirring, until the solution is alkaline to phenolphthalein. Continue to boil for 5 minutes, add a little filter-paper pulp (ashless), and set aside on a bath of boiling water for 15 to 20 minutes. Filter through a Whatman No. 42 filter-paper, keeping the contents of the beaker hot throughout, and wash the precipitate with hot wash solution (6·0 g of oxalic acid, 2·0 g of ethylenediaminetetra-acetic acid and 100 ml of saturated ammonium chloride solution diluted to 1 litre and made alkaline to phenolphthalein by adding ammonium hydroxide). Ignite the wet precipitate, and weigh the residue as R_2O_5.

For a second precipitation, wash the precipitate twice, ignite it to oxide, and re-precipitate as before. Alternatively, dissolve the precipitated hydrated oxides in a hot mixture of oxalic and hydrochloric acids, add the necessary amount of EDTA, and re-precipitate with ammonium hydroxide. In this way, ignition of the precipitated earth acids and fusion with potassium hydrogen sulphate are avoided. However, when the precipitate is dissolved from the filter-paper, the solution must be free from any filter-paper fibres (otherwise, after boiling the acid solution to make it clear, precipitation of earth acids may be incomplete).

Table IV

Amounts of earth acids found in prepared mixtures

Amount of TiO_2 present, mg	Amount of R_2O_5 present, mg	Amount of R_2O_5 precipitated, mg	TiO_2 content of precipitate, mg	R_2O_5 content of precipitate, mg	Error, mg
Single precipitation—					
8·3	95·0	96·1	0·8	95·3	+0·3
20·8	91·5	94·0	2·0	92·0	+0·5
Two precipitations—					
50·0	73·6	74·5	0·6	73·9	+0·3
	73·6	73·9	0·4	73·5	−0·1
	83·5	83·4	0·3	83·1	−0·4
	94·3	96·1	1·3	94·8	+0·5
98·0	81·4	82·1	1·0	81·1	−0·3
100·0	83·5	84·7	1·3	83·4	−0·1

Discussion of results

Table IV shows the results obtained when prepared mixtures of the oxides of earth acids and titania were analysed by the proposed method.

Separation was not improved when precipitation was carried out in the cold, the pH being carefully controlled at 8·5 ± 0·1, and the mixture was then boiled; indeed, more titania was carried down by the earth acids. During precipitation from hot solution, the addition of a little more ammonium hydroxide did not result in any appreciable increase in the titania content of the earth acids, *i.e.*, critical control of pH is not essential. If the amount of titania present in any mixture was twice that of the earth acids or more, over 75 per cent. of the titania was co-precipitated with the earth acids.

The proposed method is similar in efficiency to the methods mentioned previously,[2 to 8] but it is easier to carry out and so forms a good preliminary step to the separation of niobium from tantalum by other methods.

We thank Mr. M. Sankar Das for useful discussions during the progress of the work.

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Received *June 9th*, 1959

An Improved Method for the Determination of Small Amounts of Sulphate

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A procedure is described for the determination of small amounts of sulphate in high-purity chemicals.

The sample is digested with a titanium - phosphoric acid reagent, which reduces sulphate ion to sulphide. The hydrogen sulphide produced is swept from the reaction flask by a stream of carbon dioxide and absorbed in sodium hydroxide solution. The determination is completed by titrating the sulphide with standard mercuric acetate solution, diphenylthiocarbazone being used as indicator.

It is possible to determine 10 μg of sulphate in a wide range of substances to an accuracy of within ±10 μg.

Methods for determining trace amounts of sulphate that depend on the precipitation of barium sulphate suffer from various disadvantages, not the least of which is that the solubility of barium sulphate in many electrolytes is unknown.

Samuelson[1,2,3] has shown that interfering cations may be removed by passing the solution through a column containing an ion-exchange resin of the sulphonic acid type (hydrogen form). The only cation in the effluent is the hydrogen ion, and the determination may be carried out with greater precision than on the original solution. If a turbidimetric end-point is used, the limit of detection of sulphate is 100 μg in 50 ml of solution.

A method for the indirect flame-photometric determination of sulphate has been described[4] in which the sulphate is precipitated by a known amount of barium, the barium

sulphate is removed by centrifugation and the excess of barium is determined. The limits claimed are 0 to 70 p.p.m.

Schroeder[5] developed a procedure for determining sulphate by titrating against barium chloride solution with tetrahydroxyquinone as indicator. The method is accurate to within 3 per cent., with a lower limit of about 30 mg per litre. The end-point is difficult to detect and the indicator is not particularly stable.

A method for the titrimetric determination of sulphate, in which ethylenediaminetetraacetic acid (EDTA) was used to titrate the excess of barium added in known amount to precipitate the sulphate was described by Sijderius.[6] It will be appreciated that this method is of value only when there are no metals present that form a complex with EDTA. The method is widely used for determining sulphate in boiler waters.

Benzidine hydrochloride[7 to 11] solution has been used to precipitate sulphate quantitatively; the benzidine sulphate formed can then be titrated against standard sodium hydroxide solution with phenolphthalein as indicator. The accuracy of the method is at best to within 0·5 to 1 per cent.; it decreases rapidly with increasing acidity and with increasing electrolyte content.

The turbidimetric method of determining sulphate can be improved by adding a seeding agent,[12,13] and this method has been recommended in Addendum I (1952) to the Danish Pharmacopoeia (1948), in the Norwegian Pharmacopoeia (1939) and, with slight modification, in the Hungarian Pharmacopoeia (1954).

Polson and Strickland[14] describe a method of determining sulphur in microgram amounts by reduction of sulphate in a stream of hydrogen and hydrogen chloride. In our method, no preliminary separations need be carried out, and no specialised apparatus is required. The method will determine down to 10 μg of sulphate to an accuracy of within ± 10 μg.

Experimental

Several techniques were investigated before deciding on the final method. A paper-chromatographic method was tried, in which a drop of the solution under test was placed on absorbent paper, freed from interfering ions and sprayed first with barium chloride solution and then with sodium rhodizonate. In theory, this should have given a white spot in a red background of barium rhodizonate. This method was found to be insufficiently sensitive.

Barium chloranilate has been used as a reagent for sulphate.[15] Barium sulphate is precipitated, liberating free chloranilic acid, which is determined spectrophotometrically. This method was tried, but the results were inconsistent, probably owing to the effect of the major constituent.

Reduction to sulphide and determination of the product—

A titanium - phosphoric acid reagent has been used to reduce sulphate to sulphide.[16] In the original method a temperature of about 300° C was employed, and the hydrogen sulphide produced was swept from the reaction flask by a stream of carbon dioxide and absorbed in 0·1 *N* iodine. The excess of iodine was determined with 0·1 *N* sodium thiosulphate. This method was tried without modification on known amounts of standard sulphuric acid in the reaction flask, but it was not possible to achieve the desired results.

Several alternative procedures were tried for determining the sulphide, including a colorimetric lead sulphide end-point and a polarographic method. The procedure finally chosen, which was shown to work well, was titration of the sulphide with an extremely dilute standard solution of mercuric acetate, diphenylthiocarbazone being used as indicator.[17]

The sample was decomposed as before with titanium - phosphoric acid reagent, the hydrogen sulphide being swept by a stream of carbon dioxide into an absorber containing 10 ml of 5 *N* sodium hydroxide, 5 ml of water and 10 ml of acetone. The solution from the absorber was washed into a small conical flask, and a little more sodium hydroxide was added to ensure alkalinity, since a considerable amount of sodium carbonate was formed by absorption of carbon dioxide. The sulphide was titrated with 0·001 *M* mercuric acetate, a few drops of a 0·1 per cent. solution of diphenylthiocarbazone in acetone being used as indicator.

A sharp colour change was obtained at the end-point, the colour of the solution changing from pale yellow to pink during an addition of 0·04 ml of titrant.

During the course of the preliminary experiments with this method, some modifications were made. It was found that complete evolution of hydrogen sulphide was aided by the

addition of a little water to the reaction mixture, and a temperature of about 200° C maintained for 20 minutes gave encouraging results. By starting with known amounts of standard sulphuric acid in the reaction flask, recoveries of between 90 and 110 per cent. were obtained for between 100 and 300 μg of sulphate.

The quantity and the concentration of sodium hydroxide solution used in the absorber were altered to allow for the distillation of a certain amount of water from the reaction flask and to permit a smaller absorber to be used.

It was found unnecessary to add acetone to the absorbent solution, as the titration usually proceeded equally satisfactorily without it. However, it does have the effect of intensifying the colour change to some extent, which is useful when an unusually large amount of sulphide is obtained.

Method

Apparatus—

A 50-ml conical flask with a ground-glass neck is required, fitted with a Dreschel-bottle top shortened so that the inlet tube does not touch the surface of the reaction mixture. The inlet tube is connected to a source of air-free carbon dioxide, and the exit tube leads to a suitable absorption vessel of about 10-ml capacity. It is important that the products of the reaction shall not come into contact with rubber tubing. For this reason it is advisable to have a suitable length of glass tubing leading straight from the reaction vessel to the absorber.

Reagents—

Titanium - phosphoric acid reagent—Warm 5 g of metallic titanium (sponge or turnings) with 200 ml of AnalaR orthophosphoric acid until solution is complete (4 to 5 hours).

Carbon dioxide, air-free—From a cylinder or suitable generating apparatus.

Mercuric acetate, approximately 0·001 M—Prepare from an accurate weight of mercuric acetate of known purity.

Diphenylthiocarbazone indicator solution, 0·1 per cent. w/v, in acetone.

Sodium hydroxide solution, 50 per cent. w/v and 5 N.

Procedure—

Prepare the apparatus for use as described below.

Transfer 10 ml of titanium - phosphoric acid reagent and 3 ml of water to the 50-ml flask, and connect to the carbon dioxide supply. Pass a steady stream of carbon dioxide through the flask for about 2 minutes. Maintain the flow of carbon dioxide, heat the contents of the flask to boiling, boil gently for 30 minutes, and then set aside to cool.

The reagent is now ready for use; it can be used for three or four successive tests.

Accurately weigh an appropriate amount of sample, and transfer to the reaction flask (100 μg of sulphate will give a titre of just over 1 ml). Wash round the inside of the flask with about 3 ml of water.

Place 3 ml of 50 per cent. w/v sodium hydroxide solution and 2 ml of water in the absorber, and connect to the exit tube from the reaction flask. Connect the inlet tube to the carbon dioxide supply, and pass a steady stream of carbon dioxide through the apparatus at a rate of about two bubbles per second for 2 minutes. Maintain this flow rate carefully during the reaction.

Heat the contents of the flask gently to boiling, and boil gently for 30 minutes. Disconnect the absorber, and transfer its contents quantitatively to a small conical flask, keeping the volume as small as possible.

Add 3 or 4 drops (not more) of diphenylthiocarbazone indicator solution and 5 ml of 5 *N* sodium hydroxide, and titrate with 0·001 *M* mercuric acetate until the colour of the solution changes from pale yellow to pink. A burette calibrated down to 0·02 ml should be used.

1 ml of 0·001 *M* mercuric acetate $\equiv$ 0·096 mg of sulphate.

Results

The method was used on a variety of compounds. For each, a known amount of standard sulphate solution was added to the sample in the reaction flask, and the determination was carried out as described. A blank determination was also carried out on the compound.

without the addition of standard sulphate, so that the result could be corrected for sulphate already present.

Recoveries of added sulphate lay between 88 and 110 per cent., except with nickel oxide, for which an exceptionally high blank value was obtained.

TABLE I

DETERMINATION OF SULPHATE BY THE PROPOSED METHOD

Compound	Amount of compound taken, g	Amount of compound taken, ml	Sulphate added μg	Total sulphate found, μg	Added sulphate recovered, μg	Recovery, %
Sodium carbonate decahydrate	1·0	–	0	27	—	—
	1·0	–	120	132	105	88
	0·5	–	200	200	186	93
Hydrochloric acid	—	1	0	16	—	—
	—	1	100	110	94	94
	—	2	150	165	133	89
Sodium chloride	0·2	–	0	20	—	—
	0·2	–	100	125	105	105
	1·0	–	200	300	200	100
Orthophosphoric acid	—	1	0	70	—	—
	—	1	100	165	95	95
	—	1	200	260	190	95
Acetic acid	—	1	0	10	—	—
	—	1	100	100	90	90
	—	1	200	195	185	93
Lead acetate	1·0	–	0	10	—	—
	1·0	–	100	120	110	110
	1·0	–	200	210	200	100
Nickel oxide	0·1	–	0	330	—	—
	0·1	–	100	450	120	120
	0·2	–	100	830	130	130

INTERFERENCES

The method was not expected to succeed with certain classes of compounds, and several of these were investigated.

(*a*) *Compounds containing oxidising anions*—Anions such as chlorate, bromate and dichromate cause oxidation of the titanium - phosphoric acid reagent, thereby preventing the reduction of sulphate to sulphide.

Nitrates behave in a similar manner. Bromides interfere, probably owing to the liberation of free bromine.

(*b*) *Barium compounds*—It was thought that reduction of barium sulphate to sulphide might prove difficult in view of the insolubility of the former, although Suzuki, Harimaya, Tsuji and Yamaoka did not report any difficulty.[16] The method was tried on samples of barium chloride to which known amounts of sulphate had been added.

It was found necessary to employ a longer heating time than usual, 45 minutes being necessary to attain a recovery of 90 per cent.

It is recommended that a longer heating period should be employed for all compounds of barium.

(*c*) *Silver compounds*—These were examined as it was thought that the insolubility of silver sulphide in concentrated acids might prevent the quantitative liberation of hydrogen sulphide.

The method was tried on silver carbonate, with known amounts of added sulphate, and good recoveries were obtained after the normal heating time on samples weighing not more than 0·5 g. With larger samples, recovery was incomplete, and a residue of metallic silver was found in the reaction flask, due to reduction by titanous ion.

(*d*) *Mercury compounds*—Mercuric chloride was examined and was found to interfere. Some mercuric chloride appeared to pass over into the absorption vessel, where it reacted with the sulphide formed.

(*e*) *Compounds of metals in a high valency state*—Compounds containing metallic ions readily reduced to a lower valency state interfere by oxidation of the titanous ion in the reagent. Even cupric salts behave in this way, and recoveries of only 40 per cent. could be obtained for added sulphate in cupric chloride.

Conclusions

The proposed method offers a means of determining traces of sulphate down to 10 μg with an error of the order of ± 10 μg in a wide range of substances. It should be applicable to practically all materials that neither possess oxidising properties in the presence of the titanium - phosphoric acid reagent nor give rise to oxidising products. Certain compounds, such as those of mercury, interfere because the metal ion passes into the absorption vessel.

The method gives more reliable results than a turbidimetric test in which a suspension of barium sulphate is compared with suspensions produced by sulphate solutions under standard conditions.[18] By the latter procedure, it was often impossible to obtain a precipitate of barium sulphate from as much as 100 μg of sulphate in 50 ml of solution when an electrolyte was present. Sometimes, for larger amounts of sulphate, the recovery was as low as 50 per cent. when compared with the turbidity of an equivalent amount of sulphate without an electrolyte.

The apparatus required for the proposed procedure is simple, and the method is straightforward, requiring no special skill on the part of the analyst. A single determination may be completed in about 35 minutes, and the manipulating time is not more than 10 minutes.

This paper is published with the permission of the Directors of The British Drug Houses Limited, and we thank Mr. G. F. Lewis for help and assistance in preparing the paper and Mr. W. T. Elwell, Chief Analyst of Imperial Chemical Industries Limited, Metals Division, for providing titanium metal with a low sulphur content.

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Received *August 31st*, 1959

The Precipitation of Basic Bismuth Formate from Homogeneous Solution and the Determination of Bismuth in Presence of Lead

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The precipitation of basic bismuth formate from homogeneous solution by hydrolysis of urea has been studied. Dense and readily filterable precipitates have been obtained, permitting large amounts of material to be handled. The method has been applied to the determination of bismuth in presence of lead by igniting the precipitate to oxide. Errors caused by adsorption and occlusion were found to be negligible.

THE precipitation of basic bismuth formate by adding sodium formate and formic acid to a suitably neutralised solution of bismuth and lead has been described by Benkert and Smith.[1] The method was tedious and two re-precipitations were necessary before separation was complete. Kallmann[2] re-examined the method; he replaced sodium formate by a 40 per cent. solution of ammonium formate and paid particular attention to the pH at which precipitation was carried out. Silverman and Shideler[3] have criticised Kallmann's modification when applied to the determination of large amounts of bismuth (about 0·5 g) in presence of lead. They reported that the precipitate was too difficult to handle and that separation was not complete after two re-precipitations.

Since many examples have been given of the superior results obtained by precipitation from homogeneous solution,[4,5] it was considered that the application of this technique to the precipitation of basic bismuth formate might overcome the difficulties experienced by previous workers. By carrying out precipitation from homogeneous solution, local concentrations of the precipitating ion are avoided and the reaction occurs at a slow controllable rate. This results in the formation of dense and readily filterable precipitates, and fewer errors are caused by adsorption and occlusion.

The object of this investigation was to follow the course of the reaction under homogeneous conditions, to study the effect of variations in the concentrations of the reactants and to apply the method to the determination of bismuth in presence of lead.

Experimental

Formic acid and urea were added to a solution of bismuth in nitric acid. When boiled, the urea was hydrolysed, liberating ammonia and carbon dioxide, the pH of the solution slowly increased and basic bismuth formate was precipitated in a dense and filterable condition. Samples were removed at intervals from the boiling reaction mixture, chilled to stop the reaction and then filtered. Their pH values were recorded. The amount of bismuth remaining in solution in each sample was determined by direct titration with a solution of ethylenediaminetetra-acetic acid, pyrocatechol violet being used as indicator.[6] Precipitation was carried out both in presence and absence of formic acid, and the effects of varying the concentrations of formic acid and urea were studied. The precipitates formed during the reactions were collected and their compositions were determined.

Apparatus—

The reactions were carried out in a 1-litre flask fitted with a reflux condenser and heated with a bunsen burner adjusted to maintain a gentle rate of boiling. All pH values were measured with a Pye Universal pH meter, a glass electrode and a wick-type calomel electrode being used. Readings were taken to the nearest 0·05 unit of pH. Calibrated apparatus was used when preparing stock solutions and taking samples for analysis.

Reagents—

Spectrographically pure bismuth was used; lead and all other reagents were of analytical-reagent grade. Stock solutions of bismuth and lead were prepared by dissolving 10 g of the metal in 50 ml of nitric acid, sp.gr. 1·42, and diluting to 1 litre with distilled water.

EFFECT OF FORMIC ACID—

Solutions were prepared by dissolving the required amount of urea in 250 ml of stock bismuth solution, adding the necessary amount of 90 per cent. formic acid and diluting to 550 ml with distilled water. In the absence of formic acid, 10 g of urea were sufficient; in presence of 20 and 40 ml of formic acid, the amount of urea was increased to 50 g and in presence of 60, 80 and 100 ml of formic acid, 100 g of urea were used. This increase was necessary to permit the reactions to be completed in a reasonable time. The results were expressed graphically by plotting the weight of bismuth remaining in solution against pH.

The reaction was first carried out in the absence of formic acid. Most of the bismuth present at the start of the reaction was precipitated at a constant pH of about 0·75 (see Fig. 1). Towards the end of the reaction the pH began to increase, slowly at first, and then at an uncontrollable rate to a value above 7·0 as the last traces of bismuth were precipitated. The precipitate was finely divided and difficult to filter; when formed in a solution containing a few drops of bromocresol green indicator solution, particles of adsorbed dye were visible on the surface. The reaction in the absence of formic acid was clearly unsuitable for use in the separation and determination of bismuth.

The presence of formic acid had a pronounced effect on the course of the reaction (see Fig. 1). The pH at which precipitation started increased with the formic acid concentration; the pH no longer remained constant during the initial stages of precipitation, and relatively large increases in pH, necessitating long periods of boiling, were needed to complete the precipitation. Further, there was a period during which precipitation of bismuth slowed down or ceased until the pH had reached a markedly higher value. This was particularly evident in the reactions carried out at the higher concentrations of formic acid.

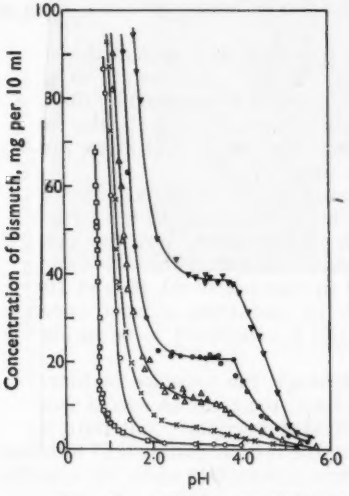


Fig. 1. Effect of different amounts of formic acid on precipitation of bismuth: □, no formic acid; ○, 20 ml; ×, 40 ml; △, 60 ml; ●, 80 ml, ▼, 100 ml

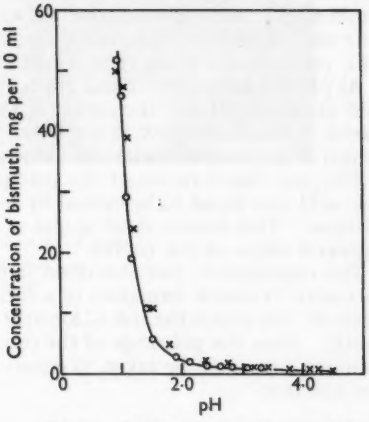


Fig. 3. Effect of urea on precipitation of bismuth: ○, 20 g of urea; ×, 50 g of urea

Dense white precipitates, readily ignited to bismuth oxide, were obtained from solutions containing up to 40 ml of formic acid. These precipitates settled more rapidly and were more easily filtered than those obtained by Kallmann's method.[2] Fig. 2 shows a comparison of the results obtained when equal amounts of bismuth were precipitated by hydrolysis of urea and by Kallmann's method. In presence of more than 60 ml of formic acid a greyish discoloration was noticeable; this became more pronounced at higher concentrations of formic acid. These precipitates were more finely divided.

EFFECT OF UREA—

Two solutions, one containing 20 and the other 50 g of urea, were prepared in the way described above; both solutions contained 40 ml of 90 per cent. formic acid in a total volume of 550 ml. The results were expressed graphically, as before, by plotting the weight of bismuth remaining in solution against pH (see Fig. 3).

COMPOSITION OF PRECIPITATES—

Examination of the infra-red spectra showed the presence of nitrate and hydroxyl groups in all precipitates, the peaks diminishing as the concentration of formic acid in the reaction solution was increased. All precipitates formed in the presence of formic acid were shown to contain formate, and their nitrate and formate contents were determined; the results were—

Amount of formic acid in solution, ml ..	Nil	20	40	60	80	100
Formate content of precipitate, % ..	0·0	3·5	5·2	4·4	5·0	5·5
Nitrate content of precipitate, %	3·5	1·3	1·4	0·5	n.d.	n.d.

DISCUSSION OF RESULTS—

The curves in Fig. 3 indicate that variation in the amount of urea present has no significant effect on the course of the reaction.

In absence of formic acid the pH rapidly increases, except when the solution is gently heated, and the precipitate formed is finely divided. The hydroxyl ions formed in solution during hydrolysis of urea are removed by formation of the insoluble basic bismuth precipitate; provided, therefore, that the solution is gently heated and that a slow rate of urea hydrolysis is maintained, the increase in pH is checked for a time. When only a small amount of bismuth remains in solution, however, the pH increases at an uncontrollable rate, even with gentle boiling.

In presence of formic acid the rate of increase in pH is slowed down, presumably owing to a buffering action caused by formation of ammonium formate; this results in a denser precipitate. When the ratio of formic acid to bismuth in solution is increased by the addition of more formic acid, precipitation begins at a higher pH. Since this ratio is also increased during the reaction by removal of bismuth from solution, the formic acid being present in excess, precipitation at no time occurs over a constant range of pH.

At pH values between 2 and 2·5 in the higher concentrations of formic acid, precipitation ceased until the pH had increased by about 1 unit. This is attributed to the formation of a soluble bismuth complex at the lower pH, the complex being stable up to the higher pH, at which it breaks down with the subsequent completion of precipitation.

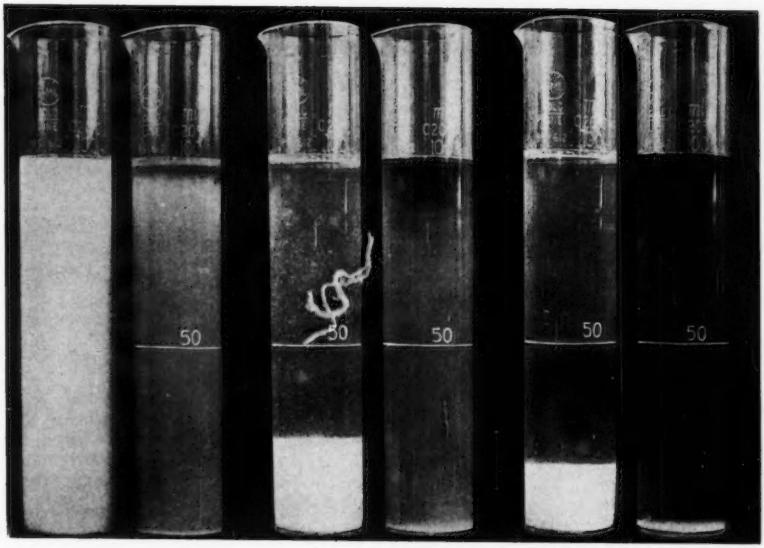
The grey discoloration of the precipitate observed in presence of 60, 80 and 100 ml of formic acid was found to be caused by metallic bismuth, *i.e.*, reduction occurred under these conditions. This occurs at all stages of precipitation and is considered to be incidental to the general shape of the curves.

The experiments just described indicated that, although the presence of formic acid is necessary to ensure formation of a satisfactory precipitate, too great an excess should not be present; this avoids the risk of forming a more finely divided precipitate containing metallic bismuth. Since the pH range of the reaction depends on the ratio of formic acid to bismuth in solution, care must be taken to ensure that precipitation is complete under the conditions of the reaction.

DETERMINATION OF BISMUTH IN ABSENCE OF LEAD

A stock solution of bismuth was prepared as previously described and its bismuth content was checked by the oxyiodide method of Strebinger and Zins.[7] Measured portions of this solution were transferred by pipette to 400-ml beakers, and diluted to about 200 ml with distilled water. To the contents of each beaker were added 2·5 ml of formic acid and 10 g of urea. It was necessary to use unscratched beakers, as the precipitate adhered to the sides of the vessel and, if deposited in scratches, could only be removed with difficulty.

The solutions were heated with a bunsen burner and a gentle rate of boiling was maintained, distilled water being added from time to time to make up for evaporation losses. Tests for completeness of precipitation were made with a 10 per cent. aqueous solution of thiourea as external indicator, a yellow colour being formed in presence of dissolved bismuth.



(*a*) (*b*) (*a*) (*b*) (*a*) (*b*)

1 minute 10 minutes 40 minutes

Fig. 2. Precipitation of equal amounts of bismuth:
(*a*) by Kallmann's method
(*b*) by urea hydrolysis

[To face p. 218

Precipitation was always complete below pH 4·5. The use of an external indicator was subsequently abandoned; instead, a few drops of bromocresol green indicator solution were added to the reaction solution and boiling was continued until the colour of the hot solution changed to bluish green in the pH range 4·5 to 5·0.

The solutions were filtered hot through weighed porcelain crucibles (porosity No. 4), and the precipitates were washed with warm distilled water and dried in an oven at 105° to 110° C. Ignition to the oxide required cautious heating to avoid losses, owing to the rate at which conversion took place. Final ignition was carried out at approximately 500° C until constant weight was attained, the residues were weighed, as Bi_2O_3, and the bismuth contents were calculated. The results of a series of determinations are shown in Table I.

TABLE I

RECOVERY OF BISMUTH IN ABSENCE OF LEAD

Amount of bismuth present, mg	Amount of bismuth found, mg	Recovery, %
469·0	468·1	99·81
	469·0	100·00
	468·0	99·79
234·5	234·1	99·83
	234·3	99·91
	234·0	99·79
112·6	112·1	99·56
	112·6	100·00
	112·4	99·82

Precipitates were always dense and crystalline, and no difficulty was experienced in filtering and washing.

DETERMINATION OF BISMUTH IN PRESENCE OF LEAD

Various amounts of a stock solution of lead, prepared as described under "Reagents," were added to measured volumes of bismuth solution containing known weights of bismuth. Each solution was diluted to 200 ml with distilled water, 2·5 ml of formic acid and 10 g of urea were added, and the bismuth was precipitated as described previously. After ignition to oxide and weighing, the residues were examined for the presence of lead.

EXAMINATION OF RESIDUES—

A portion of the residue was dissolved by gently warming it in the minimum amount of glacial acetic acid, and the solution was diluted with an equal amount of distilled water. From 1 to 2 ml of a 10 per cent. aqueous solution of potassium dichromate were added, producing a yellow precipitate, 5 ml of acetic acid were then added, and the mixture was gently warmed. If a clear solution resulted it was taken to indicate that no measurable amount of lead was present, since lead chromate is insoluble in acetic acid. To each clear solution so obtained, 1 or 2 drops of a 0·1 per cent. solution of lead nitrate were added; a precipitate was always formed, thus indicating the general validity of the test.

The presence of lead was also tested for by using sodium rhodizonate solution.[8] An approximately 50-mg sample of the residue was placed on a crucible lid, 1 or 2 drops of 50 per cent. v/v nitric acid were added, and the mixture was evaporated to dryness, but not ignited. When cool, a few drops of a tartrate buffer solution (pH 2·79) were added and mixed with the residue by means of a glass rod. One drop of this solution was placed on a filter-paper, and then 1 drop of a 0·2 per cent. w/v solution of sodium rhodizonate was added. The results of a series of determinations are shown in Table II.

These results show that, after one precipitation, the amount of lead in the residue has been reduced to a level at which it can only be detected by a sensitive spot test. It is therefore clear that the homogeneous method of precipitation provides a dense and easily handled precipitate and permits an effective separation of bismuth from lead without the need for re-precipitation.

TABLE II

RECOVERY OF BISMUTH IN PRESENCE OF LEAD

Lead was not detected in any residue by the potassium dichromate test

Amount of bismuth present, mg	Amount of bismuth found, mg	Recovery, %	Amount of lead in precipitate, as shown by rhodizonate test
In presence of 100 *mg of lead—*			
469·0	468·7	99·94	Trace
	468·3	99·85	
234·5	234·4	99·99	
	234·1	99·83	
94·14	94·20	100·06	
	94·00	99·85	
In presence of 500 *mg of lead—*			
469·0	468·7	99·94	Slight trace
	469·1	100·00	
94·14	93·92	99·77	Trace
	94·36	100·23	

METHOD FOR DETERMINING BISMUTH IN PRESENCE OF LEAD

The solution should contain 100 to 500 mg of bismuth in presence of up to 500 mg of lead and should be sufficiently acid to prevent formation of a precipitate while being heated to boiling-point. The initial volume of the solution should be approximately 200 ml, and this volume should be maintained throughout the precipitation by occasionally adding distilled water. A clean and unscratched beaker should be used.

Add to the solution 2·5 ml of formic acid, 10 g of urea and a few drops of bromocresol green indicator solution. Heat to boiling-point with a bunsen burner, and maintain a gentle rate of boiling until the colour of the hot solution changes to bluish green (pH about 5·0).

Filter hot through a weighed porcelain crucible (porosity No. 4) or a Gooch crucible, and wash the precipitate with warm distilled water. Dry the crucible and precipitate in an oven at 105° to 110° C, cautiously ignite to the oxide, and continue to heat at approximately 500° C until constant weight is attained. Weigh the residue as bismuth oxide, Bi_2O_3, and calculate the amount of bismuth present.

I thank Mr. D. W. Wilson of Sir John Cass College for his encouragement and help and Dr. D. B. Powell for his assistance with the infra-red measurements. The work described forms part of a thesis approved for the degree of M.Sc. in the University of London.

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Received *June 25th*, 1959

Notes

A MODIFIED ALUMINON REAGENT SOLUTION

In the determination of aluminium by aluminon it is well known that great care must be taken in the preparation and storage of the aluminon - buffer composite reagent solution. Even so, the solution may be unstable and the results obtained by its use may not be reproducible. Craft and Makepeace[1] remark on the instability of the composite solution; Luke and Braun[2] mention the different behaviour of various grades of aluminon and stress the need for a commercially available grade having constant composition and purity.

All our recent supplies of aluminon have formed cloudy solutions, in which a precipitate forms on storage, and the work described here was done on a typical sample of this material. Our usual method of preparing the reagent solution has been as described below—

Dissolve 500 g of ammonium acetate in water, filter, and dilute the filtrate to 1 litre, pouring the water through the filter-paper. Add 80 ml of glacial acetic acid, 1 g of aluminon dissolved in 50 ml of water and then 2 g of benzoic acid dissolved in 20 ml of methanol. Dilute to 2 litres with water.

Dissolve 10 g of gelatin in 250 ml of hot water, dilute with 500 ml of cold water, and filter. Cool, and dilute to 1 litre. Gradually add the 2 litres of aluminon solution, with constant stirring.

The main difficulty presented by this reagent solution was experienced during the colour-development heating process in both calibration and test. Evaporation at the liquid surface caused irregular concentration of the coloured compound on the glass just above the surface. This colour was not always evenly dispersed in the final solution, which became cloudy if it contained more than 40 μg of aluminium per 100 ml.

Experimental

In an attempt to disperse the colour, acetone was added to the solution after heating. This was effective, but subsequent results were not reproducible. It was found that a second heating period after the addition of acetone helped in the dispersion and gave better reproducibility, but acetone was lost because of its high volatility. Other solvents tried were ethanol and *iso*propyl alcohol; the latter gave the best results.

The method adopted for the heating process was—

Adjust 20 ml of solution, containing from 10 to 20 μg of aluminium, and 2 ml of 5 per cent. thioglycollic acid solution to the pale-pink colour of *m*-cresol purple (pH 2·0). Add 1 ml of a 0·1 per cent. solution of Triton (a wetting agent marketed by the Rohm and Haas Company, Philadelphia, U.S.A.), 10 ml of *iso*propyl alcohol and then 15 ml of aluminon reagent solution prepared as described above. Mix by swirling, and heat in a boiling-water bath for 2 minutes. Add 20 ml of cold water (20° ± 1° C), mix by gently swirling, and heat in the boiling-water bath for a further 3 minutes. Remove the flask and its contents from the bath, set aside for 5 minutes, and cool to about 30° C in a beaker of cold water (cooling takes about 5 minutes). Add 10 ml of *iso*propyl alcohol, and keep the mixture at 20° C for 20 minutes. Dilute to 100 ml with water, and set aside for 5 minutes. Measure the absorption in a 2-cm cell with a Spekker absorptiometer (Ilford No. 604 filters).

When this method and our normal aluminon - buffer composite reagent solution were used, calibration graphs were reproducible on the same day, but not necessarily from day to day, even when the same batch of reagent solution was used. As we had shown that the method could be improved by using *iso*propyl alcohol, we decided to study the effect of incorporating this alcohol in the reagent solution.

Preparation of modified reagent solution—

Dissolve 500 g of ammonium acetate in water, filter, and dilute the filtrate to 1 litre, pouring the water through the filter-paper. Add 80 ml of glacial acetic acid, 1 g of aluminon dissolved in 100 ml of water and then 2 g of benzoic acid dissolved in 300 ml of analytical-reagent grade *iso*propyl alcohol. Add 450 ml of *iso*propyl alcohol, and dilute to 2 litres with water.

Dissolve 10 g of gelatin in 250 ml of hot water, dilute with 500 ml of cold water, and filter. Make up to 1 litre, transfer to a 3-litre beaker, and gradually add the 2 litres of aluminon solution, with constant stirring.

The final solution should be clear and should remain so when cooled and set aside; store it in a polythene bottle in the dark.

Results

Because of the slightly changed composition of the reagent solution, it was necessary to reduce the amount of *iso*propyl alcohol added at the beginning of the heating process to 6 ml, but apart from this the method was the same as before.

A fresh batch of modified reagent solution was used in the preparation of a calibration graph for aluminium contents up to 40 μg; the figures obtained are shown in Table I. This graph and the same batch of reagent solution were used in the determination of 10-μg amounts of aluminium added to separate portions of a test solution. Out of seven results, there were three values of 10·0, three of 10·2 and one of 10·3 μg of aluminium. This is an indication of the high degree of reproducibility attainable at this low level.

After storage for 1 month in a polythene bottle in the dark, the reagent solution was used to prepare another calibration graph; the figures obtained are also shown in Table I. During this time, the solution had not altered in appearance, and comparison of the figures for the two calibrations shows that negligible deterioration had occurred.

Table I

Results used in preparing calibration graphs

Amount of aluminium added, μg	Initial calibration		Calibration 1 month later	
	Absorptiometer-drum reading	Difference	Absorptiometer-drum reading	Difference
0	0·965	—	0·955	—
10	0·893	0·072	0·882	0·073
20	0·822	0·143	0·812	0·143
30	0·750	0·215	0·745	0·210
40	0·690	0·275	0·690	0·265

Conclusions

The stability of the aluminon - buffer composite reagent solution has been improved by adding *iso*propyl alcohol. The modified reagent solution is clear and appears to remain so indefinitely.

Calibration graphs for low aluminium contents are reproducible for at least 1 month from the time the stabilised reagent solution is prepared.

In repeated tests on a solution having an extremely low aluminium content a high degree of reproducibility was attainable.

We thank the Chairman and Board of Directors of Magnesium Elektron Ltd. for permission to publish this Note.

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Received *July 29th*, 1959

POLAROGRAPHIC DETERMINATION OF THIOCYANATE ION

In connection with some kinetic investigations, a method was required for determining thiocyanate ion in acidic solutions also containing hydrogen cyanide, hydrogen peroxide and sulphate ion. Most of the standard methods cannot be used under these conditions, and a polarographic method was developed.

Kolthoff and Lingane[1] have stated that thiocyanate ion de-polarises a dropping-mercury electrode reversibly to give a well formed anodic wave; the half-wave potential depends on concentration and is reported to be +0·18 volt against a saturated-calomel electrode for 10^{-3} *M* thiocyanate in "neutral or only weakly alkaline medium." We have confirmed this for neutral solutions with 0·1 *N* potassium nitrate as supporting electrolyte. An anodic wave due to cyanide was also observed under the same conditions, corresponding approximately to that reported by

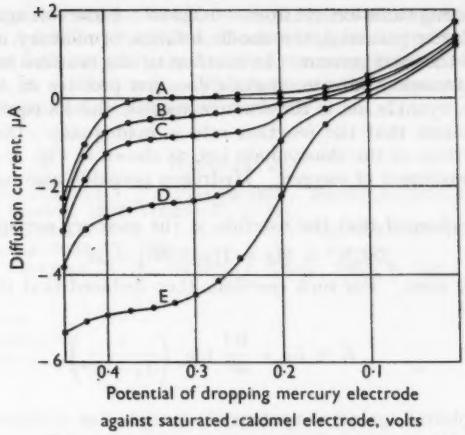

Fig. 1. Polarograms for thiocyanate ion in 0·1 *N* perchloric acid: curve A, supporting electrolyte; curve B, 10^{-4} *M* thiocyanate ion; curve C, 2×10^{-4} *M* thiocyanate ion; curve D, 5×10^{-4} *M* thiocyanate ion; curve E, 10^{-3} *M* thiocyanate ion

Kolthoff and Lingane.[1] These workers, however, used dilute solutions (10^{-2} to 10^{-1} *N*) of sodium hydroxide to suppress hydrolysis and decrease loss of hydrogen cyanide. We have found that the rate of loss of hydrogen cyanide from solution in 0·1 *N* potassium nitrate is slow, *e.g.*, less than 10 per cent. in 30 minutes with a brisk stream of nitrogen bubbling through the cell, at concentrations of about 3×10^{-4} *M*. It was therefore not possible to remove cyanide from our samples by this method.

It has been found, however, that 0·1 *N* perchloric acid is a satisfactory supporting electrolyte for this determination (see Fig. 1). Potentials at which the diffusion current due to thiocyanate

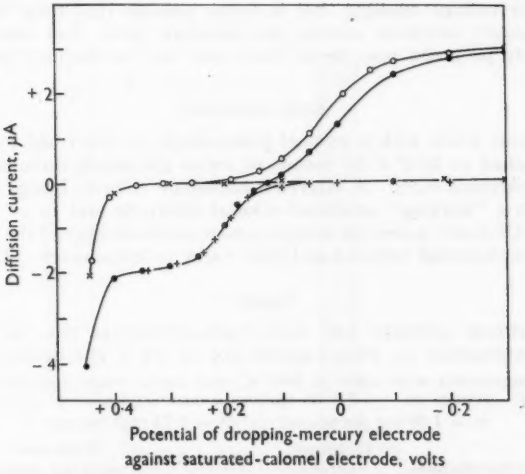

Fig. 2. Effect of oxygen on polarograms for thiocyanate ion: ×, oxygen-free 0·1 *N* perchloric acid; ○, air-saturated 0·1 *N* perchloric acid; +, 5×10^{-4} *M* thiocyanate ion *plus* 0·1 *N* perchloric acid, both oxygen-free; ●, 5×10^{-4} *M* thiocyanate ion *plus* 0·1 *N* perchloric acid, both air-saturated

ion approximates to a limiting value extend from +0·325 to +0·350 volt against a saturated-calomel electrode. Beyond the latter potential, the anodic solution of mercury in the chosen supporting electrolyte contributes to the total current. In contrast to observations in acetate buffer solutions at pH 4·6 and in 0·1 *N* potassium nitrate, cyanide does not produce an anodic wave under these conditions. Presumably, cyanide ion is the reactive species, and its equilibrium concentration is so low in the acidic medium that the reaction rate is inadequate. Dissolved oxygen did not influence the diffusion current of the thiocyanate ion, as shown in Fig. 2, and measurements were normally made without exclusion of oxygen. Hydrogen peroxide also had no effect under these conditions.

Kolthoff and Miller[2] claimed that the reaction at the mercury surface was represented by—

$$2SCN^- + Hg \leftrightharpoons Hg(SCN)_2 + 2e$$

under the conditions they used. For such reactions they deduced that the wave could be represented by the equation—

$$E = E_0 + \frac{RT}{2F} \log_e \left(\frac{i}{(i_d - i)^2} \right).$$

When $\log\left(\frac{i}{(i_d - i)^2}\right)$ was plotted against the potential a straight line of slope 0·038 volt was reported. The departure of this slope from the theoretical value (0·030 volt) was attributed to the formation of several complex ions at various points on the wave. We have also found the graph to be almost linear, with a slope of 0·043 volt, which approximately agrees with that found by Kolthoff and Miller. However, a graph of $\log\left(\frac{i}{i_d - i}\right)$ against potential could also be linear, within the accuracy of our results.

The equation for the wave quoted above requires that the half-wave potential should vary with concentration, changing by 0·030 volt for a ten-fold change in concentration. Kolthoff and Miller[2] found that the half-wave potential shifted with concentration according to this relationship. We have found that the half-wave potential, +0·205 volt against a saturated-calomel electrode in millimolar solution (as against that found by Kolthoff and Miller, +0·18 volt for a 10^{-3} *M* solution), does not show such a shift with concentration (see Table I). Our voltage readings were obtained by using an external "reference" saturated-calomel electrode.[3] It is not clear how Kolthoff and Miller[2] obtained their voltage readings, but it seems possible that they measured the potential of the dropping-mercury electrode against the mercury pool. Our results suggest that the mechanism previously proposed may be in error and that an enquiry into this mechanism is desirable.

Experimental

Measurements were made with a manual polarograph, as described by Hall and Plowman.[4] The cell was maintained at 30·0° C by means of water circulated through a water-jacket from a thermostatically controlled bath. A saturated potassium chloride bridge connected the solution being electrolysed to a "working" saturated-calomel electrode and to a "reference" saturated-calomel electrode.[3] The e.m.f. across the dropping-mercury electrode and the "reference" saturated-calomel electrode was measured with a Cambridge valve potentiometer. The capillary used was

Table I

Values of diffusion current and half-wave potential for the polarographic determination of thiocyanate ion in 0·1 *N* perchloric acid

Measurements were made at 30·0° C, and the average drop-time was 4·5(4) seconds at +0·3 volt against a saturated-calomel electrode; $m = 1{\cdot}59$ mg per second; $m^{\frac{2}{3}}/t^{\frac{1}{6}} = 1{\cdot}75$ mg$^{\frac{2}{3}}$/second$^{-\frac{1}{2}}$

Concentration of thiocyanate ion, $M \times 10^{-3}$	Diffusion current (i_d), μA	Value of $\frac{i_d}{Cm^{\frac{2}{3}}t^{\frac{1}{6}}}$	Half-wave potential against saturated-calomel electrode, volts
1·047	4·75	2·60	+0·205
0·523	2·43	2·66	+0·207
0·209	1·00	2·74	+0·210
0·105	0·48	2·61	~+0·215

a 10-cm length of barometer tubing having a uniform internal diameter of 0·05 mm. In 0·1 *N* perchloric acid and with +0·300 volt applied, the dropping-mercury electrode had a drop-time of 4·5(4) seconds and *m* was 1·59 mg per second with a mercury pressure of 30·0 cm. The diffusion currents were measured at +0·340 volt. All solutions were prepared from analytical-reagent grade materials and standardised by the usual methods.

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Received *June 22nd*, 1959

THE SEPARATION OF LEAD-212 FROM THORIUM

Gorsuch[1] has described a method for the separation of lead-212 from natural thorium in equilibrium with its decay products. This involved adsorbing the lead, bismuth, thallium and polonium on a column of De-Acidite FF and eluting the lead preferentially with 8 *N* hydrochloric acid.

It has now been found that the lead can be readily eluted with distilled water to give an extremely pure aqueous solution of the tracer.

Some De-Acidite FF anion-exchange resin of water regain 1·0 to 1·5 and −100 to +200 mesh was prepared by repeatedly washing to remove fines; it was then equilibrated with 2 *N* hydrochloric acid and packed into a column to give a resin bed 10 cm × 1·5 cm. Fifty millilitres of a thorium solution containing 10 g of thorium in 2 *N* hydrochloric acid were passed through the column, which was then washed with 25 ml of 2 *N* hydrochloric acid. The lead was eluted with distilled water. Fig. 1 shows the rapid and complete elution of the lead and Fig. 2 shows the purity of the separated material.

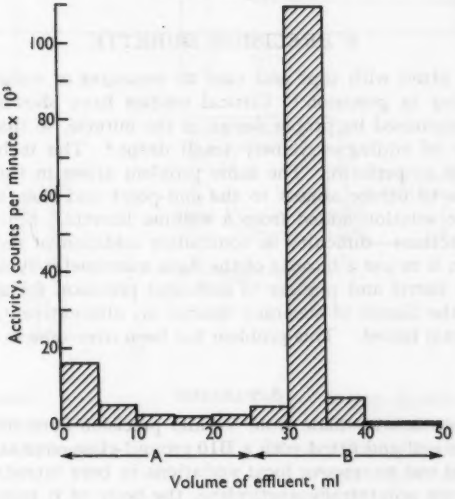

Fig. 1. Elution of lead-212 from resin column: A, with 2*N* hydrochloric acid; B, with distilled water

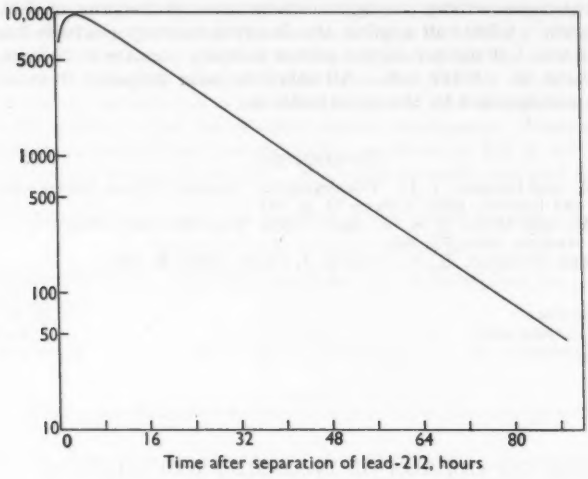

Fig. 2. Decay of separated lead-212

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Apparatus

A PRECISION BURETTE

CONVENTIONAL burettes fitted with taps and used as measures of volume have frequently been criticised as being lacking in precision.[1] Critical studies have shown that both reading and drainage errors can be minimised by proper design of the burette, so that any imprecision should arise from the difficulty of adding extremely small drops.[2] The technique of splitting drops makes a titration tedious to perform. The same problem arises in the use of weight burettes, and the usual solution is to titrate almost to the end-point and then to complete the titration with an extremely dilute solution added from a volume burette. Smith's precision burette[3] is subject to the same objections—difficulty in controlling addition of reagent.

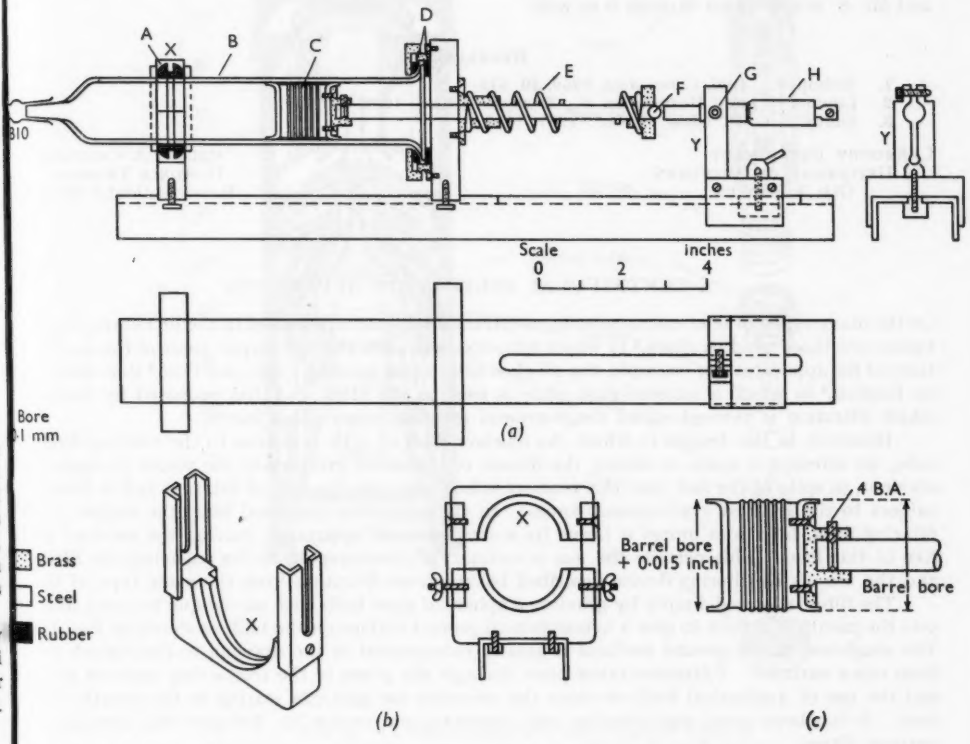
One obvious solution is to use a burette of the Agla micrometer-syringe type. The difficulty is to obtain a wide-bore barrel and plunger of sufficient precision for a micrometer-head travel of 25 or 50 mm to give the degree of accuracy desired or, alternatively, to obtain a micrometer head with more than 50 mm travel. This problem has been overcome in the apparatus described.

APPARATUS

The barrel of the burette was made from Veridia precision-bore tubing, 35·4 mm diameter, given a wide flange at one end and fitted with a B10 ground-glass cone at the other. The flanged end required to be lapped out to remove local variations in bore introduced in the working. A plunger was machined from polytetrafluoroethylene, the body of it being an accurate sliding fit in the barrel, and the forward end provided with a recessed lip 0·015 inch oversize at the tip (see Fig. 1). The plunger was mounted on a steel rod by means of a brass bracket. The barrel

and plunger were mounted and aligned by the use of steel brackets fixed to a channel-section steel baseplate. The barrel was held in place at the flanged end by two rubber washers and a threaded joint and at the other end by being clamped in a rubber grommet. The piston was mounted in a brass bush, and final alignment was made by small adjustments in the position of the barrel. The micrometer head was fixed in a clamp that could be moved along a slot in the baseplate and was brought to bear on a phosphor-bronze ball sweated into a mounting on the end of the piston. A spring was fitted to the piston to facilitate re-filling of the barrel. The liquid in the barrel was delivered through a long capillary jet attached by means of a B10 ground-glass socket and dipping into the solution to be titrated, which was stirred continuously by a magnetic stirrer.

The burette was filled initially by holding it vertically and pouring in solution through the cone. The jet was then fitted and filled with liquid by rotating the micrometer head. When the jet was full, the burette was returned to the horizontal position, in which it could be re-filled simply by rotating the micrometer head backwards with the jet dipping into the filling liquid. Any small air bubbles trapped at the lip of the plunger were removed by introducing a large air bubble to sweep them up and then removing the large bubble. After some time a small amount of liquid might seep past the plunger, but no error from this source during titrations was detected.



A = 1½-inch rubber grommet.
B = Veridia tube, 35·4 mm bore.
C = Polytetrafluoroethylene plunger.
D = Rubber washers.
E = Spring, $\frac{1}{16}$-inch diameter wire, 20 turns.
F = Phosphor-bronze ball.
G = Allen cup head.
H = Micrometer head.

Fig. 1. Diagram of burette: (*a*) complete assembly; (*b*) detail of grommet holder (not to scale); (*c*) detail of plunger (not to scale)

After the initial trials the micrometer head was fitted with a 2-inch diameter knurled knob (not shown in Fig. 1) to make turning and control easier. It was found to be quite easy to control the addition of reagent to 0·002 ml, and the burette could be read with this precision. The burette was calibrated at 5-mm intervals on the micrometer head by weighing the amount of water delivered. The maximum spread of results found in the calibrations carried out by two operators was 0·016 ml; the standard deviation for any volume delivered was calculated to be 0·004 ml. The total volume delivered was 23·18 ml, with a spread of 0·011 ml in the calibration (eight results). Replicate titrations were made with ammonium ferrous sulphate solution against standard ceric sulphate; the maximum spread of results was 0·01 ml.

Discussion of the apparatus

Veridia tubing is guaranteed to have a maximum variation in bore of 0·01 mm. Calculation shows that, with 35·4-mm tubing, a precision of 1 in 1770 or better should be attainable (if micrometer errors are ignored); this precision was attained in practice for volumes of about 20 ml. For delivery of larger volumes it would be necessary to obtain a micrometer head with longer travel. The main advantage of the apparatus is the high degree of control over the addition of reagent and the ease with which the titration can be terminated at the exact end-point.

We thank Mr. A. Barclay for his valuable help in designing the apparatus and Mr. H. Harris and Mr. S. Weathers for making it so well.

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A CENTRIFUGAL FILTRATION APPARATUS

Of the many types of semi-micro centrifugal filtration apparatus described in the literature, the best known are those used by Skau,[1] in which filtration is usually through paper, some of the modifications of his apparatus, for example, the all-glass filter tubes used by Craig and Post,[2] that described by English,[3] in which a sintered-glass plate is used as the filter, and that proposed by Bush,[4] in which filtration is through short rough-ground standard-taper glass joints.

However, in the designs in which the receiver flask or tube is similar to the filtering flask or tube, no attempt is made to relieve the former of the extra pressure of the pieces of apparatus above it, in spite of the fact that this receiver is furthest from the axis of rotation and is therefore subject to the greatest gravitational forces. In the apparatus described here, the weight of the filtering flask, filter and funnel is borne by a stainless-steel apparatus, leaving the receiver flask free of this load. This permits the use of ordinary Erlenmeyer flasks for receiving the filtrate, and the use of the filtering device described below allows filtration from the same type of flask.

The filter is formed simply by grinding a spherical glass bulb with an oblique twisting motion into the mouth of a flask to give a hemispherical ground surface on the bulb as shown in Fig. 1 (*a*). The roughness of the ground surfaces is greatly exaggerated in the drawing to distinguish them from other surfaces. Filtration takes place through the pores of the contacting surfaces at AA, and the use of a spherical bulb obviates the necessity for accurate seating in the mouth of the flask. It has been found that grinding with carborundum powder No. 220 gives the best general-purpose filters.

The hemispherical ground surface may be conveniently formed on the bulb by a preliminary grinding with a glass tube of approximately the same diameter as the neck of the flask, and then this bulb is ground lightly into the mouth of the flask. This ensures that the ground ring on the lip of the flask is not too wide, because if it extends to the edge of the lip the jagged edge that results may cause cracks to appear in the glass.

Obviously this type of ground filtering surface can be put on to any type of flask or vessel. It has been found useful to have it on top of a standard-taper ground-glass joint in the neck of a

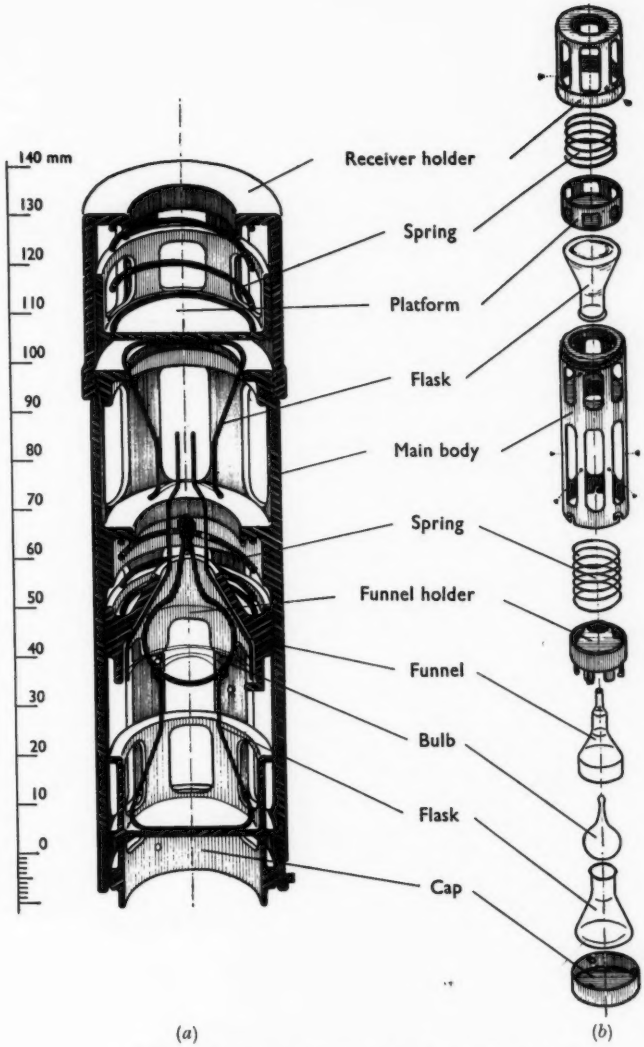

Fig. 2. Complete apparatus (the cap and flask in (*a*) are not the same as those in (*b*); the cap shown in (*a*) is used with 5-ml flasks and that shown in (*b*) is used with 10-ml flasks)

[To face p. 228

round-bottomed flask if filtering is required from a crude reaction mixture, the flask having been used with a reflux condenser, for instance, for the reaction. Flasks with filtering bulbs are shown in Fig. 1(*b*).

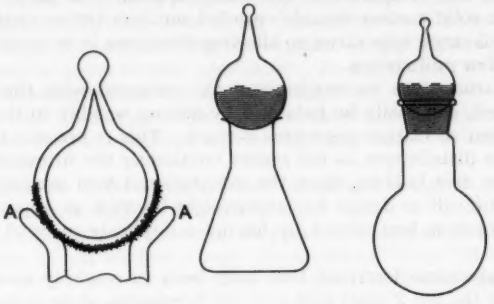

Fig. 1. (*a*) Filtering bulb; (*b*) flasks used with filtering bulbs

For filtration, the flask with its bulb is placed in an apparatus that serves to hold the bulb firmly against the mouth of the flask by means of a spring-loaded glass funnel, as shown in Fig. 2 (*a*). The apparatus shown is of stainless steel and was designed to take 5- or 10-ml Erlenmeyer flasks, depending on the cap being used. The apparatus is also capable of filtering from 10-ml round-bottomed flasks with B14 sockets. In Fig. 2 (*a*) 5-ml flasks are shown, and in Fig. 2 (*b*) 10-ml flasks are incorporated. The caps and flasks are therefore not the same in the two views of the apparatus. In assembling the apparatus for filtration, the flask with its bulb is placed on its appropriate cap and the main body of the apparatus is placed over it so that the funnel in its holder is pushed against the spring by the flask and bulb until the apparatus can be twisted into the locked position of the bayonet fitting. The receiver flask, which may be either 10 or 5 ml, is inverted into the opening at the top of the main body and the receiver holder is screwed on. In doing so the platform in the latter serves to hold the flask and align it so that the stem of the funnel is in the centre of the mouth of the flask.

The apparatus is now ready for spinning in a centrifuge. It is inverted immediately before centrifugation in the swinging-bucket type of apparatus. A rate of up to 2800 r.p.m. has been used without any breakages occurring in the glass portions, but experience has shown that centrifuge speeds in excess of 2000 r.p.m. are never necessary for complete separation of crystals and mother liquor. During centrifugation, the steel cap with the flask, bulb, funnel and funnel holder move down until the cap is held by the pins in the bayonet slots. The flask and bulb carry on downwards with the funnel and its holder until the latter comes to rest against the shoulder in the main body. At the same time the receiver flask moves down with the platform until the latter comes to rest on the bottom of its holder. The apparatus was designed so that these movements are a minimum, being of the order of a few millimetres only. When the centrifuge slows down to rest these movements are reversed.

After filtration, the receiver portion is screwed off, leaving the flask with the filtrate standing on the platform. The crystals may be rapidly dried by placing the apparatus, minus the receiver portion, in a vacuum desiccator and alternately exhausting and allowing dry air into the apparatus a few times. This serves to "wash" the crystals with air, thereby quickly removing the last traces of solvent, so that the flask with crystals and bulb may be weighed. Although a single bulb should be able to serve all flasks, in practice it is more convenient to have a separate bulb for each flask and to mark them and record their combined weight.

As the filtration and receiver flasks are interchangeable, fractional crystallisation becomes extremely simple, and at any time dust and dirt may be separated from a solution by centrifugation from one flask to another. The other advantages of centrifugal filtration will not be discussed here, as these have been adequately dealt with by the previous workers mentioned above.

The apparatus has been scaled up to take 50- and 100-ml flasks and has given satisfactory results, although with these sizes of flasks speeds above 1600 r.p.m. are not recommended, as the

receiver flasks tend to break. However, this speed is sufficient for most filtrations. Recrystallisations have been found useful on this larger scale when concentrated solutions are used, when decolorising by charcoal is required or for recrystallisations at low temperatures, *e.g.*, −70° C. For recrystallisations at low temperatures the whole apparatus is easily enclosed in a plastic bag and immersed in a solid carbon dioxide - alcohol mixture before centrifugation. Adaptors have been made to fit this larger apparatus, so allowing filtrations to be made from glass tubes with internal diameters of a few millimetres.

The smaller apparatus, since its weight is small compared with that of its holder in the particular centrifuge used, can easily be balanced by adding weights to the opposite holder, but this cannot be done when the larger apparatus is used. This is because the counterweight will not have the same mass distribution as the holder containing the filtration apparatus, resulting in unequal forces on the two holders, since the gravitational field increases outwards from the axis of rotation. It is difficult to design a counterweight for such an apparatus having a variety of fittings, and the problem is best solved by having a duplicate piece of apparatus made as a counterweight.

The two sizes of apparatus described here have been successfully used day after day by a variety of workers during the last 2 years with very few breakages, of the order of one in a thousand. These breakages have been in the lower flask, and in these instances the filtrate was easily recovered by washing out the holder with solvent.

Although the glass portions of the apparatus are extremely simple to make, the machining of the stainless-steel portion is costly. However, commercial production of these parts in metal or possibly in some strong plastic should make it available at a reasonable price.

I thank Dr. G. W. Perold, Head of the Organic Chemistry Division, for his interest and encouragement during the designing and testing of the apparatus and the Manager of this Department, Dr. T. J. W. Jorden, for permission to publish.

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Received *August 14th*, 1959

Book Reviews

Selected Methods of Analysis of Foundry Materials. Part 1. Pig Iron and Cast Iron. Pp. 97. Birmingham: The British Cast Iron Research Association. Price 17s. 6d.; $2.50.

In common with its bigger brother, B.I.S.R.A., the British Cast Iron Research Association has a Methods of Analysis Sub-Committee, and the methods given in this book represent the first part of a laboratory manual based on the considerations of this Committee. Analysts in touch with the work of this Research Association will remember the excellent little book "The Sampling and Chemical Analysis of Cast Ferrous Metals," prepared by E. Taylor Austin, issued by the Association in 1941 and also the much larger volume sponsored by the Association, "Chemical Analysis of Cast Iron and Foundry Materials," by Westwood and Mayer, published in 1951. The book under review is not intended as a replacement for either of the two earlier publications; indeed, work has begun on a new edition of the 1951 book. It is described in the foreword by N. L. Evans, Chairman of the Methods of Analysis Sub-Committee, as a laboratory manual; the whole is to comprise four parts, and there will follow—The Analysis of Alloy Cast Irons and Ferro-alloys; Slags, Refractories and Fuels; Methods for Residual Elements. We are also told that "In order to make the manual as concise as possible and suitable for use at the bench, the subject matter has been restricted to the practical details of each method. More theoretical aspects are already dealt with in textbooks such as Westwood and Mayer."

The first section is on sampling; sections 2 to 11 deal in turn with the determination of carbon, silicon, manganese, sulphur, phosphorus, nickel, chromium, molybdenum, copper, titanium and vanadium. Sections 12, 13 and 14 deal with the spectrophotometric determinations of manganese, of manganese, nickel, chromium, copper and molybdenum in a single sample and of titanium and vanadium (and silicon). There is little in the first eleven sections to arouse comment. The methods, it is claimed, have been exhaustively investigated by the Methods of Analysis Committee and will give reliable results under routine conditions. In the chapter on sulphur, three methods are given, but there is no indication as to their relative merits. On p. 55, more specific directions could have been given with advantage as to the temperature of precipitation of molybdenum by means of benzoin oxime; it is not perhaps sufficiently realised that a low temperature results in a much purer precipitate.

In the last three sections suitable photometric procedures are given for the determination of all the elements except carbon, sulphur and phosphorus.

Information about equipment, apparatus, reagents and laboratory techniques is given in an appendix. The reviewer would challenge only the statement that "platinum crucibles are too expensive to allow of their being used for large batches of determinations." This needs some qualification according to circumstances.

On the whole this is a well arranged book and will no doubt be useful in the foundry industry. The reviewer would have preferred to see some attempt at stating briefly the principles on which each method was based, as in the 1941 booklet. One is tempted to ask who is to carry out these analyses, for if he has not some chemical intelligence, a cookery book will of itself be inadequate, and if he has chemical intelligence, ought it not to be fostered and stimulated?

In spite of these minor criticisms this industry and some others are to be congratulated for their organised efforts at analytical self-help and for making available the results of their co-operative efforts.

R. C. CHIRNSIDE

QUALITATIVE ANALYSIS AND ELECTROLYTIC SOLUTIONS. By EDWARD J. KING. Pp. xxiv + 641. New York: Harcourt, Brace and Company Inc. 1959. Price $6.95.

In many universities and technical colleges, the teaching of qualitative analysis stands at a cross-roads, for there is a movement afoot to dispense with it altogether in favour of courses in physical and inorganic chemistry. Qualitative analysis should be, and usually is, taught not as an end in itself, but more broadly as a means of developing a knowledge of inorganic reactions in aqueous solutions and of applying such knowledge in practice to overcoming difficulties as they are met. Qualitative analysis, however, is also necessary as the chemical detective work that must precede quantitative analysis of an unknown material. Even nowadays many industrial laboratories, for example, do not possess a spectrograph or staff skilled in its use. Training in qualitative analysis is therefore necessary as well as desirable for educational reasons. On the other hand, bookshelves are stacked to overflowing with literally hundreds of books on qualitative analysis, most of which are mediocre and sometimes completely out of touch with modern developments in inorganic and physical chemistry.

The author remarks that he has written this book with the express purpose that it should *not* be a cemetery of old theories and experimental results. He has succeeded admirably in this and has produced a text that brushes aside completely the undergrowth of stale chemistry and inadequate background that chokes up most books of this type. Interwoven with the basic straight inorganic reactions of the qualitative scheme are to be found topics such as the structure of water, hydrogen bonding, crystal structure, solution of ionic crystals, hydration of ions, electrolytic conductance, co-ordination, orbital structures, magnetic moments, reaction rates, equilibrium constants, theory of precipitation and contamination, the direction of reversible ionic reactions and so on. Within the scheme itself, the reactions are examined inside a modern framework, so that the well known precipitation and colour reactions are discussed in the light of electronic structure, ionic size, co-ordination number, standard oxidation potential, etc. The basic reactions are thus used as pegs on which to hang up-to-date knowledge and theory in a way that cannot but evoke respect and admiration.

The semi-micro scheme for cations is conventional in most respects and is well annotated and set out. The section on anions is developed as far as possible according to the same system; it makes use of the semi-systematic Belcher - Weisz scheme. The appendices teem with data on ionisation constants, solubility products, complex constants, oxidation potentials, free energies

of formation and electronic structure; the subject index is comprehensive. Throughout the text there are many numerical problems and questionnaires for student use.

I would assess this book as one marking a new departure in the writing of text-books for qualitative inorganic analysis. In its pages modern theory is related efficiently to classical qualitative analysis. No teacher of students can afford to dismiss this fresh approach to an age-old problem. For the intelligent student, the book is easy to read and assimilate, but it is somewhat unwieldy for use as a laboratory manual. This, however, is of minor importance in view of the quality and scope of the text. Verdict—one of the few books on qualitative inorganic analysis that cannot safely be ignored.

T. S. WEST

Publications Received

ANALYSTS POCKET BOOK. By J. R. MAJER, B.Sc., Ph.D. Pp. x + 100. London: Butterworths Scientific Publications. 1959. Price 17s. 6d.

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Erratum

FEBRUARY (1960) ISSUE, p. 108, 15th line from foot of page. *For* "60 = 1" *read* "601".